University of Bucharest Faculty of Chemistry ASC-UB

Students' Scientific Communications Session

- The 16th Edition -

Book of Abstracts

May 28-29th, 2021

Bucharest, Romania

UNIVERSITY OF BUCHAREST
VIRTUTE ET SAPIENTIA

ASC-UB
Asociatia Studentilor Chimisti a Universitatii din Bucuresti

University of Bucharest **Faculty of Chemistry** **ASC-UB**

Students' Scientific Communications Session

- The 16th Edition -

Book of Abstracts

May 28-29th, 2021

Bucharest, Romania

Scientific Committee

President, Prof. Dr. Andrei-Valentin Medvedovici
Vice-President, Lect. Dr. Emilia-Elena Iorgulescu
Vice-President, Lect.Dr. Delia-Laura Popescu

Evaluation Committee Members

Bachelor Level (Day 1)

Conf. Dr. Marilena Cimpoeșu
Conf. Dr. Mădălina Săndulescu
Lect. Dr. Emilia-Elena Iorgulescu
Lect. Dr. Eliza Oprea
Lect. Dr. Adina Răducan

Master and PhD Level (Day 2)

Prof. Dr. Habil Ioan Cezar Marcu
Conf. Dr. Vasile David
Conf. Dr. Bogdan Jurca
Conf. Dr. Augustin Mădălan
Conf. Dr. Christina-Marie Zălaru

Organizing committee

The Chemistry Students Association of the University of Bucharest (ASC-UB)

ASC-UB

Asociatia Studentilor Chimisti a
Universitatii din Bucuresti

Nicolae Daniel Andreiu, Project coordinator, ASC-UB

Andra-Ștefania Ene, ASC-UB

Miruna Ghiță, ASC-UB

Alexandru Bara, ASC-UB

Traian-Dinu Păsătoiu, ASC-UB

Lect. Dr. Delia-Laura Popescu, Faculty of Chemistry

www.asc-ub.ro

comunicari@asc-ub.ro

The Chemistry Students Association of the University of Bucharest (ASC-UB) acknowledges for their support:

FACULTATEA DE CHIMIE

UNIVERSITATEA DIN
BUCUREȘTI
VIRTUTE ET SAPIENTIA

GUVERNUL ROMÂNIEI
MINISTERUL EDUCAȚIEI ȘI
CERCETĂRII ȘTIINȚIFICE

BIOFARM®

Content

Section 1 – Bachelor Level **9**

Ariadna-Elena-Maria Beneş, Cătălin Maxim, Andrei A. Pătraşcu, Delia-Laura Popescu - *New extended structures of organotin(IV) with dicarboxylic acids* **11**

Cosmina Bohan, Darius Dumitraş, Alexandra Pop - *New diorganochalcogen(II) compounds. Synthesis and structural characterization* **12**

Claudia-Raluca Chivu, Adina Liana Răducan - *The Interaction Between Nimesulide and Bovine Serum Albumin: a spectroscopic study* **13**

Cristian Alin Cucu, Carmen Postolache - *Kinetic aspects of the enzymatic reaction of urea hydrolysis* **14**

Maria David, Roxana-Alexandra Popa - Group 11 metal complexes based on diorganoselenium ligands **15**

Iulia Andreea Florea, Iulia-Gabriela David, Emilia-Elena Iorgulescu - *Voltammetric Study of Epinephrine* **16**

Ana-Maria Fulgheci, Petre Ioniță, Ioana Nicolau, Irina Zarafu - *Synthesis of new heterocyclic compounds derived from ferrocene* **17**

Alina-Florentina Gonțoiu, Viorica Corbu, Sorin Marius Avramescu - *Chemical profile and antifungal activity of staghorn sumac (Rhus typhina) extracts* **18**

Oana Bianca Nedelcu, Adina Răducan - *Fluorescence quenching studies for bovine serum albumin-levofloxacin interactions* **19**

Roxana Nicorici, *Cătălina Ioniță, Marilena Ferbințeanu Cimpoeșu - Structural and Spectral Characterization of Metal Complexes with 2-Pyridyl Aldoxime* **20**

A.T. Oncescu, V. Popovici, A.M. Tencaliec, - *The assessment of heavy metals in drinking water from Ploiesti areas* **21**

Oana Petcuţă, Mihai Bordeiaşu, Mihaela Turtoi, Augustin M. Mădălan, Cătălin Maxim, Delia-Laura Popescu - *Synthesis, characterization and bioactivity of new oxidovanadium(V) complexes with Schiff base ligands* **22**

Alessandra-Diana Selejan, Ana-Maria Cormoș - *The equilibrium model of the steam reforming process using biogas as raw material for hydrogen production* **23**

Ioan Stroia, Ionuț-Tudor Moraru, Niculina D. Hădade, Ion Grosu - *Synthesis and structural investigation of novel chiral cyclophanes containing p-terphenyl units* **24**

Alexandru-Tudor Toderaşc, Adriana Urdă, Ioan-Cezar Marcu - *New highly effective transition-metal-containing MgFe mixed oxides catalysts for benzyl alcohol hydrodeoxygenation* **25**

Denisa Voinea, Mihai Răducă, Cătălin Maxim, Delia-Laura Popescu - *Novel Cobalt(II) coordination polymers constructed from 4,4'-oxy(bis)benzoic acid and N-donor ligands* **26**

Section 2 – Master Level 27

Cezara-Marina Bolocan, Mihai Răducă, Delia-Laura Popescu - *Cobalt(II) metal-organic frameworks containing dichromate and chromate anions as spacers* 29

Mihai Bordeiaşu, Mihai Răducă, Augustin M. Mădălan, Delia-Laura Popescu - *Cu(II)-based metal-organic frameworks with pillared Kagomé layers* 30

Bogdan M. Boşca, Augustin C. Moț - *Determination of selenium in biofortified Allium microsamples using selective complexation and chromatographic detections* 31

Roxana Ciorteanu, Dumitrela Diaconu, Vasilichia Antoci, Dorina Amăriucăi-Mantu, Cătălina Ciobanu, Violeta Mangalagiu, Ionel I. Mangalagiu - *Hybrid Pyridin-Benzimidazole Salts: Antimicrobial Properties* 32

Nicoleta Ana-Maria Codreanu, Adrian Popa, Dana Elena Popa, Mihaela Buleandră - *Cost-effective pencil graphite electrode for fast analysis of riboflavin and pyridoxine in pharmaceuticals* 33

Mona Georgescu, Viorica Meltzer, Elena Pincu - *Study of the binary mixtures nimesulide-salicylic acid* 34

Maria Cristina Gheţu, Mădălina Tudorache - *Bienzymatic biocatalyst for cascade transformation of monoterpenes* 35

Giulia Roxana Gheorghiță, Cristina Purcărea, Mădălina Tudorache - *Cold-active lipase biocatalysts for silymarin valorization* 36

Ana Hodorogea, Alexandra Pop - *Synthesis and coordination behaviour of new N/S/O macrociclic ligands* 37

Simona Ioniță, Daniel Lincu, Mihaela Deaconu, Ana-Maria Brezoiu, Raul-Augustin Mitran, Rodica Tatia, Cristian Matei, Daniela Berger - *Mesoporous silica - polysaccharide nanocomposites with potential biomedical applications* 38

Laura Iordache, Gabriela Iulia David - *Voltametric Study of Ferulic Acid* 39

Delia Mărtinaş, Adina Răducan - *Influence of microcomponents on the activity of horseradish peroxidase in the oxidation of Coomassie Brilliant Blue G dye with hydrogen peroxide* 40

Nimet Numan, Iulia Gabriela David - *Hesperidin voltammetric investigation at the pencil graphite electrode* 41

Cătălin Eduard Şalgău, Anca Silvestru - *Structural aspects in mercury complexes with organoselenium ligands* 42

Bianca-Alexandra Stoean, Castelia Cristea, Luiza Ioana Găină - *New contrast agents containing methylene blue analogues customized for bioimaging of cancer cells* 43

Paul Adrian Tărăbuță, Cătălin Maxim, Marius Andruh - *Discrete and polymeric complexes of CuII and ZnII with N-heterocyclic ligands* 44

Mihail-Alexandru Udrea, Ana-Maria Albu, Cristian-Andi Nicolae - *Fabrication of Doped* 45

Polyvinyl Alcohol Membranes for Use in Polymer Electrolyte Membrane Fuel Cells

Cătălina-Diana Ușurelu, Oana Maria Memecică, Ileana Brândușa Rău, Ana-Maria Albu - *Chelating Macromolecular Architectures with High Ionic Selectivity* **46**

Section 3 – PhD Level **47**

Florin Andrei, Nicu Doinel Scărișoreanu, Ioan-Cezar Marcu - *The effect of the film thickness on the photoelectrochemical properties of LaFeO3 obtained by pulsed laser deposition* **49**

Adrian A. Apostol, Teodora Mocanu, Cătălin Maxim, Oana Tutunaru, Cristina Pachiu, Marius Andruh - *Co-crystallization on graphene support* **50**

Sabina Ion, Anamaria Hanganu, Mădălina Tudorache, Vasile I. Pârvulescu - *Grafting natural lignin with aniline using biocatalytic approach* **51**

Andreia-Cristina Soare, Victor David - *Temperature dependence of the phase ratio parameter in reversed phase high performance liquid chromatography* **52**

Cristian Andrei Spinu, Celine Pichon, Gabriela Ioniță, Teodora Mocanu, Sergiu Calancea, Mihai Răducă, Jean-Pascal Sutter, Mihaela Hillebrand, Marius Andruh - *Synthesis and characterization of nitronyl nitroxide metal complexes derived from nitro-o-vanillin* **53**

Alexandra-Elisabeta Stamate, Rodica Zăvoianu, Octavian Dumitru Pavel, Ioan-Cezar Marcu - *Synthesis, characterization and catalytic activity of $Mg_3Al_{0.75}Ce_{0.25}$-LDH-GO composites* **54**

Marius C. Stoian, Ionel Popescu, Ioan-Cezar Marcu - *The effect of Co content on the catalytic performance of Co(x)-CeMgAlO ex-LDH mixed oxides in methane total oxidation* **55**

Alexandru Topor, Daniel Avram, Cătălin Maxim, Carmen Tiseanu, Marius Andruh - *Luminescence thermometry based on 1D benzoato-bridged coordination polymers containing lanthanide ions* **56**

Section 1 – Bachelor Level

New extended structures of organotin(IV) with dicarboxylic acids

Ariadna-Elena-Maria Beneş, **Cătălin Maxim, Andrei A. Pătraşcu, Delia-Laura Popescu***

University of Bucharest, Faculty of Chemistry, Department of Inorganic Chemistry, 23 Dumbrava Roşie, 020464-Bucharest, Romania

Organotin(IV) coordination polymers have received great attention due to their ability to stabilize specific stereochemistry in their complexes and to induce diverse dimensionalities, as well as to their potential application in agriculture, industry, biology, medicine [1-3].

Several new extended structures have been synthesized by slow evaporation method in the reaction of $^{n}Bu_3SnCl$ with deprotonated dicarboxylic acids: 1,4-cyclohexanedicarboxylate (1,4-chd) (**1**), adipate (adp) (**2**), fumarate (fum) (**3**), and biphenyl-4,4'-dicarboxylate (bpdc) (**4**) employed as linkers. The newly prepared compounds have been characterized by elemental analysis, infrared spectral studies, as well as single crystal X-ray diffraction. The compounds have the empirical formulas: $^{2}_{\infty}[(^{n}Bu_3Sn)_2L]$ where L = 1,4-chd (**1**), depicted in Figure 1, adp (**2**), $^{3}_{\infty}[(^{n}Bu_3Sn)_2(fum)]$ (**3**), and $[(CH_3OH)_2(^{n}Bu_3Sn)_2(bpdc)]$ (**4**). The crystal structures of the resulting assemblies have been determined and the intermolecular interactions of the compounds in the crystalline phase have been investigated.

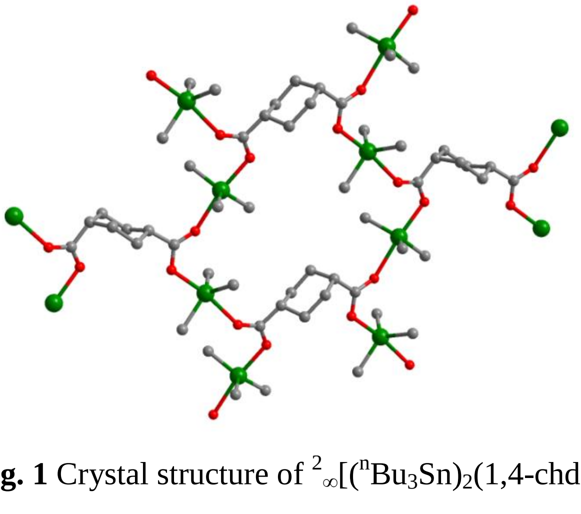


Fig. 1 Crystal structure of $^{2}_{\infty}[(^{n}Bu_3Sn)_2(1,4\text{-chd})]$

References

[1] Kadu, R.; Roy, H.; Singh, V.K. Appl. Organomet. Chem. 2015, 29, 746;
[2] Awang, N.; Zakri, N.H.; Zain, N.M., J. Chem. Pharm. Res. 2016, 8, 862;
[3] Iornumbe, E.N.; Yiase, S.G.; Sha'Ato, R. Int. J. Sci. Res. 2016, 5, 1610.

New diorganochalcogen(II) compounds. Synthesis and structural characterization

Cosmina Bohan, **Darius Dumitraş and Alexandra Pop**

Supramolecular Organic and Organometallic Chemistry Centre, Chemistry Department, Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, Cluj-Napoca, Romania

cosmina.bohan@stud.ubbcluj.ro

The chemistry of homoleptic or heteroleptic diorganochalcogen compounds (mainly sulfur and selenium derivatives) having organic groups containing nitrogen and/or oxygen as donor atoms gained a continuously increasing attention in the scientific community. This type of compounds can be used for different applications in many fields *e.g.* organic synthesis, biology, medicine, materials science and microelectronics due to their optical or electronic properties.[1][2]

Our attention was focused on the synthesis and structural characterization of heteroleptic diorganochalcogen(II) compounds containing butyl moiety attached to the chalcogen atoms. REBu type compounds (E = S, Se; R = benzaldehyde, 4-arylidene-5(4*H*)-oxazolone) were prepared and characterized 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) (Figure 1) was determined by single-crystal X-ray diffraction.

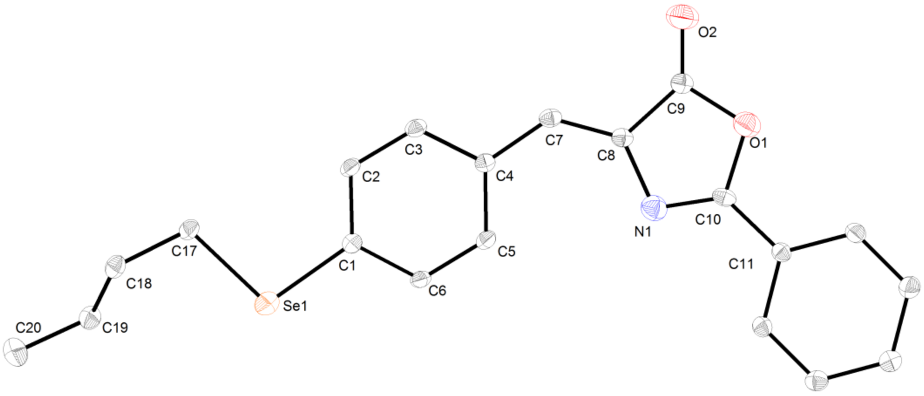


Fig. 1: Molecular structure of RSeBu

[1] G. Mugesh, H. B. Singh, Chem. Soc. Rev., **2000**, 29, 347.
[2] Y. Tabuchi, N. Sugiyama, T. Horiuchi, M. Furusawa, K. Furuhama, Eur. J. Pharmacol., **1995**, 272, 195.

The Interaction Between Nimesulide and Bovine Serum Albumin: a spectroscopic study

Claudia-Raluca Chivu, Adina Liana Răducan

Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, bd. Elisabeta 4-12

Nimesulide (NIM) is a non-steroidial antiinflammatory drug with preferential inhibitory action on the enzyme active component of the cyclooxygenase pathway (COX-2). Recently it was showed that NIM can be used for COVID19 treatment, since it abolishes the transport function of B0AT1. The receptor targeted by SARS-CoV-2 is a dimer of ACE2-B0AT1, in which ACE2 binds the viral protein and B0AT1 stabilizes the heterodimer[1].

We studied the interaction between nimesulide (NIM) and bovine serum albumin (BSA) by a range of spectroscopic techniques. Then we analyzed the binding parameters and the nature of the forces manifested during the interaction.

We measured the quenching of BSA's fluorescence in the presence of varying concentrations of nimesulide (NIM) by monitoring the fluorescence intensity in the wavelenghth range 300-400 nm, after the excitation at 280 nm. We noticed that the fluorescence quenching is mainly due to the participation of the tryptophan residues (Trp). The value of the binding constant, K_a and the number of available binding sites, n, were also estimated.

To identify the main BSA binding sites we used two methods : the classic one , by using drug markers (ibuprofen for site II and warfarin for site I) and an alternative method –by using specific dyes (malachite green for site I and methylene blue for site II). The results showed that NIM binds mainly to Sudlow's site (site I), in the subdomain IIA.

[1] Scalise M, Indiveri C. „Repurposing Nimesulide, a Potent Inhibitor of the B0AT1 Subunit of the SARS-CoV-2 Receptor, as a Therapeutic Adjuvant of COVID-19", SLAS Discov. 10, (1171-1173), 2020.

Kinetic aspects of the enzymatic reaction of urea hydrolysis

Cucu Cristian Alin, Postolache Carmen

Faculty of Biology, University of Bucharest, Splaiul Independenței Street, no. 91–95, sector 5, Bucharest, 050095

Soil urease is involved in a very specific step of nitrogen cycling. It has a particular interest in agriculture, when its activity is increased by the addition of chemical fertilizers, which leads to several negative ecological impacts such as soil pH, carbon sequestration, and greenhouse gas emissions, along with the eutrophication potential on aquatic ecosystems.

It is necessary to know the factors that influence its activity both in laboratory and field studies, in order to help promote measures that reduce the negative impact of agricultural practices. This study aims to determine several kinetic and thermodinamical parameters that characterize the urease activity, such as temperature, pH, substrate concentration and activation energies. Therefore, the laboratory analyzes were performed using two enzyme sources: *Canavalia ensiformis* (laboratory purified) and soil from Fundulea research station. The two enzymes showed different activity, pH dependences, as well as different substrate affinities and maximum reaction rates.

Group 11 metal complexes based on diorganoselenium ligands

Maria David and **Roxana-Alexandra Popa**

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

A continuously increased interest was observed during last decades for various types of organoselenium compounds, which are valuable candidates for biological and technical applications. Derivatives containing organic groups with side arms bearing nitrogen as donor atoms proved an increased thermal and hydrolytic stability, as well as improved catalytic and biological activity.[1,2]

Our recent interest was focused on the synthesis and structural characterization of silver(I) and copper(II) complexes of the neutral organoselenium ligand $[2\text{-}(Me_2NCH_2)C_6H_4]_2Se$, as displayed in Figure 1.

The as obtained silver(I) and copper(II) complexes were characterized by appropriate spectroscopic methods: multinuclear NMR, mass spectrometry, UV-Vis and IR spectroscopy, mass spectrometry and single-crystal X-ray diffraction.

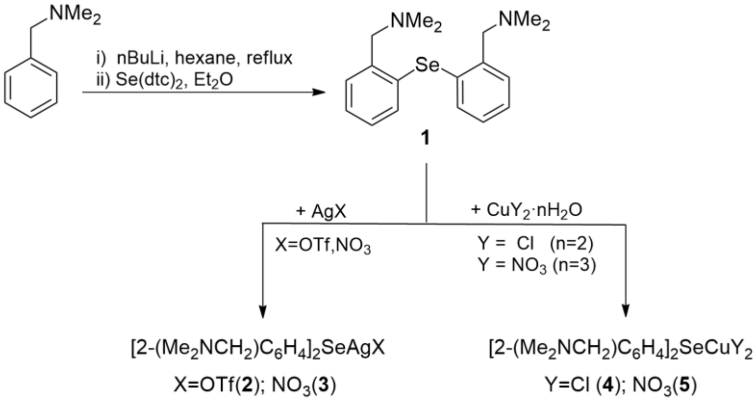


Figure 1. Reaction scheme for the synthesis of compounds **1-5**.

---

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;

Voltammetric Study of Epinephrine

<u>Iulia Andreea Florea</u>[1], Iulia-Gabriela David[1], Emilia-Elena Iorgulescu[1]
[1]University of Bucharest, Faculty of Chemistry, Department of Analytical Chemistry, 90-92 Panduri Av., 5- Bucharest, Romania

Epinephrine (known as adrenaline), EP, is one of the most important catecholamine neurotransmitter for message transfer in the mammalian central nervous system and it is released by the adrenal gland under conditions of low blood sugar levels or in reaction to psychological stresses. [1,2] It has important functions in the regulation of physiological processes in living systems, treatment of myocardial infarction, bronchial asthma, hypertension and cardiac surgery. The quantitative determination of epinephrine is, therefore, important not only in nerve physiologic functions but also for diagnostic and control in clinical medicine. [3]

Cyclic Voltammetry (CV) was used to investigate the electrochemical behaviour of EP at the surface of the glassy carbon electrode (GCE) at various scan rates and in different pH phosphate buffer solutions.

A simple differential-pulse voltammetry (DPV) method was developed for the quantitative determination of EP using a GCE at the optimum pH value of the supporting electrolyte. The DPV oxidation peak current showed a linear response to EP concentration, in the range 5.0×10^{-7} to 7.5×10^{-5} M. The effects of different potentially interfering substances on the epinephrine voltammetric signal were also studied. The proposed DPV method was applied for determination of this analyte from Adrenaline Injection using the standard addition method.

References:
[1] W. A. Banks, Brain Res., 2001, 899, 209.
[2] L. Jackson, F. L. R. Williams, A. Burchell, M. W. H. Coughtrie and R. Hume, J. Clin. Endocrinol. Metab., 2004, 89, 6251.
[3] A. A. Ensa, M. Taei and T. Khayamian, Colloids Surf., B, 2010, 79, 480.

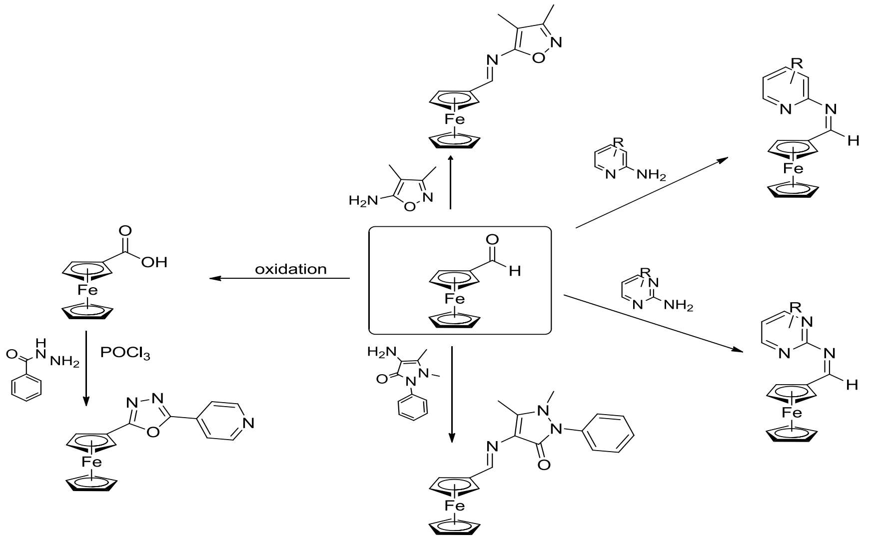
Synthesis of new heterocyclic compounds derived from ferrocene

<u>Ana-Maria Fulgheci</u>, Petre Ioniță, Ioana Nicolau, Irina Zarafu

Faculty of Chemistry, University of Bucharest, Bulevardul Regina Elisabeta, sector 3, București

Ferrocene derivatives constitute an important class of organometallic compounds, with a wide range of biological activities and various industrial applications, including material science applications; these derivatives are associated with a wide range of biological activities, such as analgesic, antineoplastic, anticonvulsant, anti-HIV, antitumor, antimalarial, antioxidant, antimicrobial, and DNA-cleaving activities, among which antitumor and antimalarial activities of ferrocene derivatives have attracted special attention [1].

In this research we report the synthesis of various heterocyclic compounds, starting from ferrocenecarboxaldehyde, and using different heterocyclic amines or hydrazides [2, 3] as coupling components, with the final aim to test the biological activity of the thus obtained compounds.



References

1) Larik, F., Saeed, A., Fattah, T., Muqadar, U., Channar, P., Recent advances in the synthesis, biological activities and various applications of ferrocene derivatives. *Appl Organometal Chem.*, (**2017**), 1:22.
2) Batsanov, A., Herault, D., Howard, J., Patrick, L., Probert, M., Whiting, A., Synthesis and Structure of Planar Chiral, Bifunctional Aminoboronic Acid Ferrocene Derivatives. *Organometallics*, 26 (**2007**), 2414:2419.
3) Neto, A., Miller, J., de Andrade, V., Fujimoto, S., de Freitas Afonso, M., Archanjo, F., Darin, V., Andrade e Silva, M., Borges, A., Del Ponte, G., New Synthesis of Ferrocene Monocarboxylic Acid and Systematic Studies on the Preparation of Related Key-Intermediates. *Z. Anorg. Allg. Chem.*, 628 (**2002**), 209:216.

Chemical profile and antifungal activity of staghorn sumac (*Rhus typhina*) extracts

Alina-Florentina Gonțoiu[1], Viorica Corbu[2], Sorin Marius Avramescu[1]

[1]Department of Organic Chemistry, Biochemistry and Catalysis,
Faculty of Chemistry, University of Bucharest
[2] Department of Genetics, Faculty of Biology, University of Bucharest,

Staghorn sumac (*Rhus typhina*) plant play a significant role in gardening and forestation these days due to his striking fall color and for the capability to grow in almost any well-drained soil. Nevertheless this type of flowering plant like any other about 35 species in the genus Rhus contain a large range of natural compounds with different antimicrobial and antioxidant activities.

This work aimed to evaluate the antifungal and antioxidant activities of extracts obtained from different parts of *Rhus typhina* (flower and leaves) using microwave assisted extraction technique.

The antifungal activity of *R. typhina* extracts was tested against several fungal species like: *Aspergillus nidulans, Aspergillus niger, Penicillium chrysogenum, Penicillium corylophilum* collected from different historical buildings. The extracts showed a strong antifungal action with a minimum inhibitory concentration (MIC) around 12.5%.

Moreover, the antioxidant activity of the extract was investigated by DPPH method and also some flavonoids, phenols, and organic acids were identified and quantified by using HPLC – DAD analytical technique.

Fluorescence quenching studies for bovine serum albumin-levofloxacin interactions

Nedelcu Oana Bianca, Raducan Adina
Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, Bd. Elisabeta 4-12, Bucharest, Romania

Proteins, an essential class of biological macromolecules, can realize their functions through binding to themselves or to other molecules. Therefore, a broad understanding of the protein–ligand interactions and their clincal implications is vital to understanding biology at the molecular level and, nonetheless, to the discovery, design, and further development of drugs. Being an extremely difficult and complex process, scientists came to the conclusion that the plasma proteins fit the best as models for in vitro analysis. Within these, serum albumin is undoubtedly the most important drug carrier. As it was extensively studied, the strong similarities between human serum albumin and bovine serum albumin made the latter more suitable for use thanks to its wider availability (as a by-product of beef industry), low cost, high aqueous solubility and stability [1].

The interaction of levofloxacin (LEVO), a xenobiotic used to treat bacterial infections, with bovine serum albumin (BSA) was studied using fluorescence quenching technique. This drug belongs to a class of therapeutic agents known as quinolone antibiotics and works by stopping the growth of bacteria.

The quenching of BSA fluorescence after adding LEVO up to a molar ratio of 1:2, showed that the interaction between the two undergoes static quenching. Using specific site markers, warfarin for site I and ibuprofen for site II, it was found that LEVO binds to the site I of BSA, also known as Sudlow site.

[1] S. Siddiqui, F. Ameen, S. ur Rehman, T. Sarwar, M. Tabish, „Studying the interaction of drug/ligand with serum albumin", J. Mol. Liq., 336, 116200, 2021

Structural and Spectral Characterization of Metal Complexes with 2-Pyridyl Aldoxime

Roxana Nicorici,[1] **Catalina Ionita,**[1] **Marilena Ferbinteanu Cimpoesu**[1]

[1] *University of Bucharest, Faculty of Chemistry, Inorganic Chemistry Department, Dumbrava Rosie 23, Bucharest 020462, Romania*

The 2-pyridyl aldoxime (paoH) is a popular ligand in the field of molecular magnetism, acting as versatile and flexible bridging ligand that can mediate magnetic exchange between paramagnetic ions. The tridentate ligand has the ability to form homo-and heteropolynuclear complexes. A strategy to form heteropolynuclear complexes is the supramolecular building blocks assembling. Therefore, in this work we present the synthesis, structural and spectral characterization of new building blocks based on paoH ligand, *mer*-$[Co(pao)_3]\cdot H_2O\cdot CH_3CN$ (**1**) 1D-$[Cu(paoH)(pao)(NO_3)]_n$ (**2**) and a collapsed 12-metallacrown-4 Cu(II) complex (**3**). The compound **1** is a mononuclear compound with a distorted octahedral geometry (Figure 1a), compound **2** is a monodimensional coordinative polymer with NO_3^- ions as bridging ligand (Figure 1b), and compound **3** is a tetranuclear complex with two different Cu coordination sites.

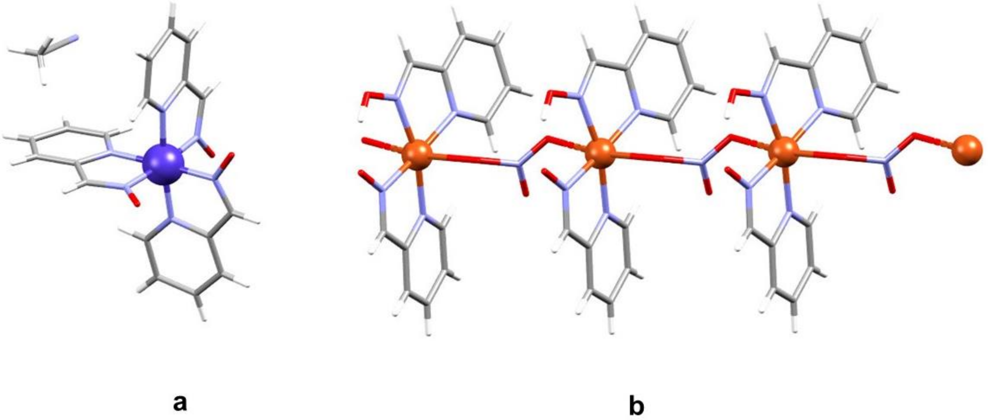


Figure 1. The molecular structure obtained by single crystal X-ray diffraction for (a) *mer*-$[Co(pao)_3]\cdot H_2O\cdot CH_3CN$ and (b) $[Cu(paoH)(pao)(NO_3)]_n$

The assessment of heavy metals in drinking water from Ploiesti areas

<u>Oncescu, A.T.</u>[1], Popovici, V.[2], Tencaliec, A. M.[1]

[1]Department of Analytical Chemistry, Faculty of Chemistry, University of Bucharest, 2-14 Blvd. Regina Elisabeta, 030018, Bucharest, Romania
[2]SC Biosol psi SRL, Str. Torcători, Nr. 6, Ploieşti, Prahova
e-mail teodoraoncescu@yahoo.ro

It is very important to ensure the continuous supply of clean and safe drinking water for the public health protection. Therefore, this study aims to assess the quality of drinking water from different sources of Ploiesti areas using inductively coupled plasma atomic emission spectrometry (ICP-OES). The concentrations obtained for iron (Fe), manganese (Mn), aluminum (Al), are listed in Table 1.

Table 1. Metal ions concentrations in drinking water from Ploiesti areas.

	Area 1	Area 2	Area 3	Area 4	UoM	MAX
Fe	<50	<50	<50	<50	μg/L	200
	<50	<50	<50	<50		
	<50	<50	<50	<50		
	<50	<50	<50	<50		
	<56	<50	<50	<50		
Mn	<1	<1	<1	1.216	μg/L	50
	<1	<1	<1	2.347		
	<1	1.049	<1	2.530		
	<1	<1	<1	2.985		
	<1.9	1.284	<1	1.475		
Al	4.342	3.610	3.316	3.009	μg/L	200
	5.634	3.380	3.120	2.983		
	3.668	4.470	3.871	5.306		
	5.986	4.125	3.417	2.185		
	3.586	3.771	3.297	2.701		

Area 1: Drinking water from the distribution area Nord Gageni, Ploiești
Area 2: Drinking water from the distribution area Crângul lui Bot, Ploiești
Area 3: Drinking water from the distribution area 23 August+Apele Române, Ploiești
Area 4: Drinking water from the distribution area Recea, Boldești Scăeni
UoM: unit of measurement; MAX; maximum admitted concentration

The results obtained by ICP-OES for Fe, Mn and Al in drinking water from Ploiesti areas are in agreement with the values prescribed by the Law 458/2002 modified and completed by the Law 311/2004.

Synthesis, characterization and bioactivity of new oxidovanadium(V) complexes with Schiff base ligands

**<u>Oana Petcuţă</u>[1], Mihai Bordeiaşu[1], Mihaela Turtoi[2],
Augustin M. Mădălan[1], Cătălin Maxim[1], Delia-Laura Popescu[1]***

[1]*University of Bucharest, Faculty of Chemistry, Department of Inorganic Chemistry, 23 Dumbrava Roşie, 020464-Bucharest, Romania*
[2]*Institute of Cellular Biology and Pathology "Nicolae Simionescu" of the Romanian Academy, 8 B.P. Hasdeu Street, 050568-Bucharest, Romania*

A new family of oxidovanadium(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 *in situ* reaction with $VOSO_4 \cdot 3H_2O$. All obtained compounds have been characterized by elemental analysis, powder and single-crystal X-ray diffraction, IR and UV-Vis spectroscopic, as well as circular dichroism measurements. The structure of Cl-sal-val enantiomers is shown in Figure 1. Vanadium compounds have shown antiviral, antibacterial, antifungal, antiobesity, antidiabetic, and antineoplastic activities, along with potential applications as antimicrobial materials in food packing and preservation [1, 2]. The stability of the obtained compounds under physiological conditions, the capacity to bind bovine serum albumin (BSA), their cytotoxicity, *as well as their potential anti-diabetic activity have been investigated and will be discussed.*

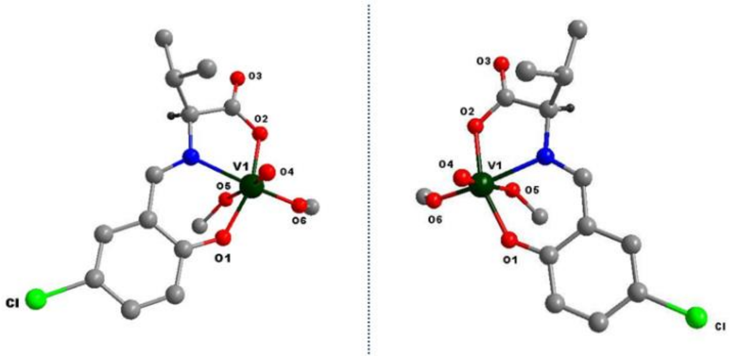


Fig.1 Crystal structure of (*S*/*R*)-[(V^VO)(Cl-sal-val)(CH_3O)(CH_3OH)]

References:
[1] K.H. Thompson, J.H. McNeill, C. Orvig, *Chem. Rev.*, **1999**, *99*, 2561.
[2] A. Scibior, L. Pietrzyk, Z. Plewa, A. Skiba, *J. Trace Elem. Med. Biol.*, **2020**, *61*, 126508.

The equilibrium model of the steam reforming process using biogas as raw material for hydrogen production

Selejan Alessandra-Diana, **Cormoș Ana-Maria**

Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University,
Cluj-Napoca, Romania, str. Arany Janos nr.11,
alessandra.selejan@gmail.com, ana.cormos@ubbcluj.ro

Being considered the future of energy due to its capacity of producing power with almost no ecological impact, hydrogen and implicitly, hydrogen's production has been intensively studied. Hydrogen's chiefly manufacturing processes are based on electrolysis and steam reforming processes from water and fossil fuels. Due to the fact that natural gas is similar in composition with the biogas and that the biogas is a renewable source, it will be further considered as the raw material for hydrogen's production in this study.

For this study it has been developed a heterogeneous model for catalytic hydrogen's production by biogas steam reforming process based on the characteristic equations. To be able to describe the equations it has been used the orthogonalization rule, which reduced the number of chemical reactions from three to two. Following this important step, the mathematical model for the mass balance has been developed. Using the mathematical model at equilibrium, the transformation rates have been calculated as functions of temperature, pressure and molar ratio of steam in the initial flow.

The kinetic model used is based on Langmuir-Hinshelwood approach and was developed by Xu and Froment for nickel-alumina spinel catalyst. Thanks to the fact that the process, in general, is highly endothermic a multi-tubular reactor with parallel tubes filled with catalyst, is used. The model has been implemented in Matlab and, in this way, the profiles for the transformation rates were obtained. Also, by using industrial data, the results have been validated.

This model will be further used to determine the energy balance and for the study of hydrogen percentage in the dry basis if changes made on the input flow's molar mass fractions may occur.

Synthesis and structural investigation of novel chiral cyclophanes containing *p*-terphenyl units

Ioan Stroia, Ionuț-Tudor Moraru, Niculina D. Hădade, Ion Grosu

Babeș-Bolyai University, Faculty of Chemistry and Chemical Engineering, 11 Arany Janos Str.,400028, Cluj-Napoca, Romania

Chiral cyclophanes are notorious for their diversity and remarkable molecular structures. Their intriguing properties (i.e. the large values of specific optical rotation, stereospecific interaction with chiral guest) and in particular their applications in supramolecular enantiomers discrimination or as chiral ligands in asymmetric synthesis have prompted researchers to develop new investigations in this field.

Herein we report synthesis, structural characterization and theoretical investigation of five macrocycles with planar chirality, that contain a dimethoxi substituted *p*-terphenyl backbone, 2, 2’’ connected by etheroxime or ether-based bridges of different lengths (Figure 1).

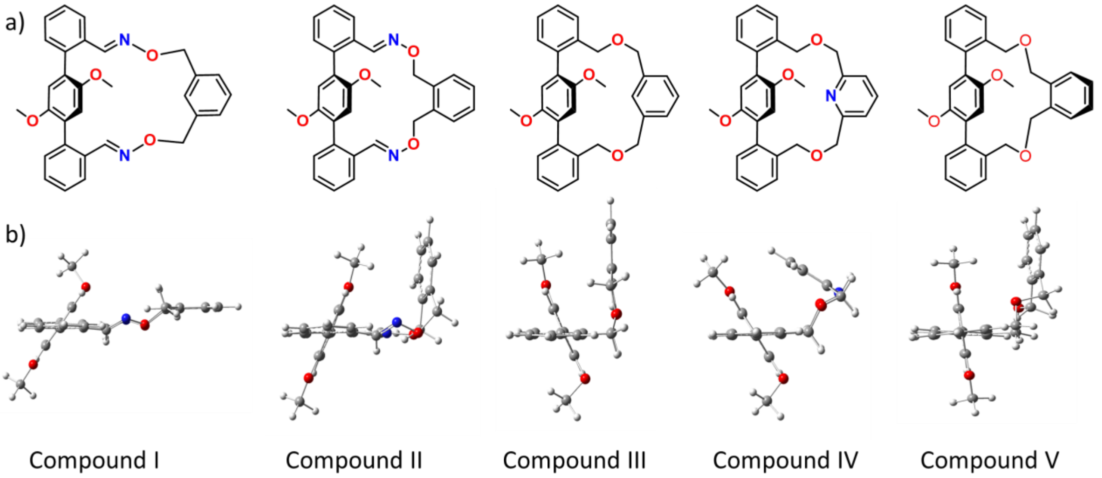


Figure 1: Representation of the synthetized macrocycles (a) and their ground state equilibrium geometries - side view (b).

New highly effective transition-metal-containing MgFe mixed oxides catalysts for benzyl alcohol hydrodeoxygenation

Alexandru-Tudor Toderașc, **Adriana Urdă and Ioan-Cezar Marcu**

Laboratory of Chemical Technology and Catalysis, Department of Organic Chemistry, Biochemistry and Catalysis, Faculty of Chemistry, University of Bucharest, 4-12, Blvd. Regina Elisabeta, 030018 Bucharest, Romania

Nowadays, hydrodeoxygenation (HDO) is employed for converting oxygenated compounds into hydrocarbons through treatment at moderate temperatures and pressures by means of C-O bond scission.[1] Copper-containing mixed metal oxides seem to be interesting catalysts for this kind of reactions due to their significant hydrogenolysis activity and limited propensity for complete hydrogenation of aromatic substrates.[2]

In this work, several transition-metal-containing M-MgFeO mixed oxides, with M = Cu, Ni, Co, Ag or Ce, were tested in the HDO reaction of benzyl alcohol. Their corresponding layered double hydroxides (LDH) precursors were prepared through coprecipitation at a constant pH of 10 using Mg, Fe and M nitrates as starting materials. The synthesized LDH were dried and then calcined at 500 ^{0} C for 5 h. The obtained mixed oxides were tested in the aforementioned reaction in an autoclave reactor at 230 ^{0} C, under 5 atm of H_2 for 3 hours. Their catalytic performance strongly depended on both the nature and the content of transition metal. Among them, Cu-MgFeO with 10 at.% Cu gave the best results, with 93,8 % alcohol conversion and 93,8 % selectivity for toluene. The influence of temperature, reaction time and catalyst loading on its performance has also been studied. Based on the products observed, a reaction pathway has been proposed.

References:

1. Rizescu, C., Sun, C., Popescu, I., Urdă, A., Da Costa, P., Marcu, I-C., *Catal. Today,* 366 (**2021**), 235:244
2. Deutsch, K.L., Shanks, B.H., *Appl. Cat. A Gen.,* 447-448 (**2012**), 144:150

Novel Cobalt(II) coordination polymers constructed from 4,4'-oxy(bis)benzoic acid and N-donor ligands

Voinea Denisa[1], **Mihai Răducă**[1], **Cătălin Maxim**[1],
Delia-Laura Popescu[1]*

[1]*University of Bucharest, Faculty of Chemistry, Department of Inorganic Chemistry, 23 Dumbrava Roşie, 020464-Bucharest, Romania*
denisa.voinea@s.unibuc.ro, delia.popescu@chimie.unibuc.ro

Systematic studies of the self-assembly process between $Co(ClO_4)_2{\cdot}6H_2O$, 4,4'-oxy(bis)benzoic acid (oba) ligand, and different rodlike N,N′-donor building blocks, such as 4,4'-bipyridyl (bipy) and 1,2-bis(4-pyridyl)ethylene (bpe), have been carried out in order to investigate the influence of dicarboxylate and N-donor ligands on the properties and construction of coordination frameworks. New coordination polymers, ${}^{1}_{\infty}\{[Co_2(oba)_2(bipy)(H_2O)_4]{\cdot}2H_2O{\cdot}4CH_3CN\}$ (**1**), ${}^{3}_{\infty}\{[Co_2(oba)_2(bipy)_2(H_2O)]{\cdot}2H_2O\}$ (**2**), ${}^{3}_{\infty}\{[Co(oba)(bpe)(H_2O)_2]{\cdot}4H_2O\}$ (**3**), and ${}^{3}_{\infty}\{[Co_2(oba)_2(bpe)_2]\}$ (**4**) were successfully obtained by slow evaporation method. The resulted compounds have been characterized by elemental analysis, X-ray diffraction on both single-crystal and powder, as well as different spectroscopic techniques, such as FTIR and UV-Vis in solid state. They exhibit diverse structures with dimensionalities 1-D and 3D, of which **1** shows a 1-D double-chain structure linked by bipy ligands, as depicted in Figure 1. The results revealed that the flexible dicarboxylate and N-donor auxiliary ligands are effective building blocks in constructing coordination polymers with diverse architectures.

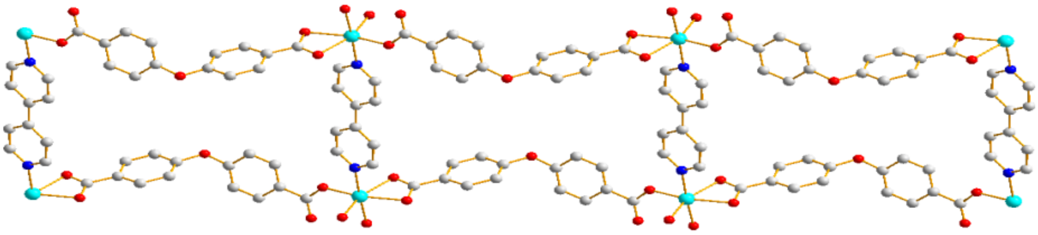


Fig. 1 Extended structure of 1-D coordination polymer **1**.
Hydrogen atoms and crystallization molecules have been omitted for clarity.

Section 2 – Master Level

Cobalt(II) metal-organic frameworks containing dichromate and chromate anions as spacers

Cezara-Marina Bolocan[1], Mihai Răducă[1], Delia-Laura Popescu[1*]

[1]*University of Bucharest, Faculty of Chemistry, Department of Inorganic Chemistry, 23 Dumbrava Roşie, 020464-Bucharest, Romania*

Extensive research has been devoted to the synthesis and characterization of MOFs due to their large area of applications. MOFs are, for instance, very good in storing, separation and transportation of gases, water absorption, catalysis, luminescence, magnetism, and drug delivery.[1-3]

New MOFs were synthesized using different salts of cobalt(II), 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), along with $Cr_2O_7^{2-}$ and CrO_4^{2-} as spacers. The obtained compounds have been characterized in solid state by elemental analysis, single-crystal and powder X-ray diffractions, different spectroscopic techniques, such as FTIR and UV-Vis, as well as thermal analysis. The new synthesized compounds present neutral tridimensional networks with various topologies. One example is represented in Fig.1.

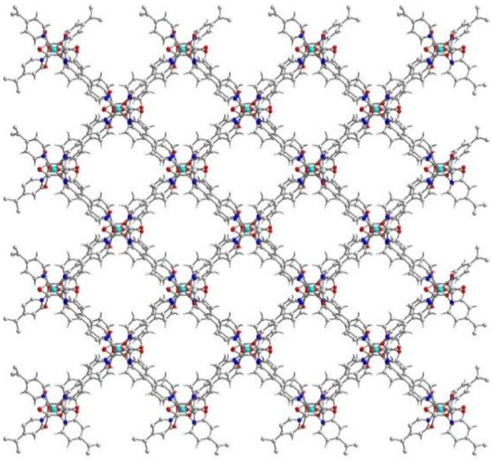


Fig.1. Crystal-structure packing model of $[Co(bipy)_2(Cr_2O_7)]_n$

References:

[1] A.K. Renfrew, E.S. O'Neill, T.W. Hambley, E.J. New, *Coord. Chem. Rev.,* **2008**, *375,* 221;

[2] R.J. Kuppler, D.J. Timmons, Q.-R. Fang, J.-R. Li, T.A. Makal, M.D. Young, D. Yuan, D. Zhao, W. Zhuang, H.-C. Zhou, *Coord. Chem. Rev.*, **2009**, *253,* 3042;

[3] B. Sareeya, J. Satoru, K. Susumu, *Sci. Technol. Adv. Mat.*, **2008**, *9*, 014108.

Cu(II)-based metal-organic frameworks with pillared Kagomé layers

Mihai Bordeiaşu, **Mihai Răducă, Augustin M. Mădălan,**
Delia-Laura Popescu*

University of Bucharest, Faculty of Chemistry, Department of Inorganic Chemistry, 23 Dumbrava Roşie, 020464-Bucharest, Romania

Pillared layer metal-organic frameworks (MOFs) display specific structural properties, such as: high regularity, porosity, tunable size and shape of pores and/or channels, great surface area etc. which make them good candidates in catalysis, biomedicine, sensing and detection, magnetism, adsorption, separation and storage of gases [1, 2].

Three-dimensional Cu(II)-based MOFs were obtained using $Cu(ClO_4)•6H_2O$ or $Cu(BF_4)•6H_2O$ salts and different exo-bidentate bipyridine-based ligands, such as: 1,2-bis(4-pyridyl)ethane (bpe), 1,2-bis(4-pyridyl)ethylene (bpy), and 4,4'-azopyridine (azopy). The general formula of the synthesized compounds is $\{[Cu_3(CO_3)_2(L)_3](Y)_2\}_n$, where L = bipyridine-based ligand and Y = ClO_4^- or BF_4^- anions. Single-crystal and powder X-ray diffraction, elemental and thermal analyses along with spectroscopic techniques, e.g. FTIR and UV-Vis in solid state, were used in characterization of these compounds. All obtained compounds are isostructural. The 2-D Kagomé layers are formed in the basic ammonia solution, by direct fixation of atmospheric CO_2 as carbonate anion and are stacked one onto another, connected via the bipyridine-based ligands, forming hexagonal channels. Disordered counter anions are found along the channels. The influence of the organic ditopic ligands used as pillars between the 2-D Kagomé layers on the size of the formed cavities, as well as the adsorption properties of these compounds are discussed.

References

1. C. Janiak, J.K. Vieth, *New J. Chem.*, 34(11) (2010), 2366-2388.
2. H.C. Zhou, J.R. Long, O.M. Yaghi, *Chem. Rev.*, 112(2) (2012), 673-674.

Determination of selenium in biofortified *Allium* microsamples using selective complexation and chromatographic detections

Bogdan M. Boșca, Augustin C. Moț

Chemometrics and Bioanalytical Chemistry Laboratory, Analytica Research Center, Department of Chemistry, Faculty of Chemistry and Chemical Engineering, Babeș-Bolyai University, 11 Arany János Street, RO-400028 Cluj-Napoca, Romania

Selenium is an essential trace element naturally distributed in all compartments of the environment. In comparison to other micronutrients, there is a much thinner line between the normal concentration and the toxic intake of selenium for 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 and selective method is demanded for detection of selenium compounds in biological samples. A distinct technique is represented by the formation of piazselenol from the reaction between an aromatic *o*-diamine and Se (IV) in acidic conditions (Figure 1). This study describes an HPLC-based optimized, sensitive and selective method for determination of selenium in biofortified *Allium* microsamples. Molecular absorption UV-Vis analysis of piazselenol formation has also been performed, 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 method. 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. Also, excellent values for coefficient of determination have been obtained.

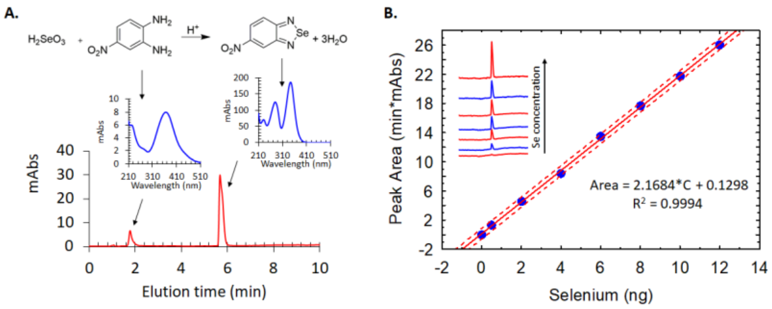


Figure 1. A. Piazselenol formation and determination by HPLC and UV-Vis techniques following solid phase microextraction step. B. Calibration curve for selenium determination based on chromatographic analytical response.

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

References

(1) Francesconi, K. A.; Pannier, F. Selenium Metabolites in Urine: A Critical Overview of Past Work and Current Status. *Clin. Chem.* **2004**, *50*, 2240–2253.

Hybrid Pyridin-Benzimidazole Salts: Antimicrobial Properties

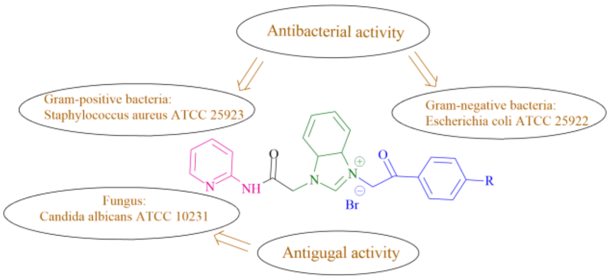
<u>Roxana Ciorteanu</u>[a]*, Dumitrela Diaconu [a], Vasilichia Antoci[a], Dorina Amăriucăi-Mantu[a], Cătălina Ciobanu[b], Violeta Mangalagiu[b], Ionel I. Mangalagiu[a,b]*

[a]*Alexandru Ioan Cuza University of Iasi, Chemistry Department, Bd. Carol 11, 700506 Iasi -ROMANIA*
[b]*Alexandru Ioan Cuza University of Iasi, Institute of Interdisciplinary Research- CERNESIM Centre, Bd. Carol 11, 700506 Iasi - ROMANIA*
**e-mail* ionelm@uaic.ro; roxana.ciorteanu@chem.uaic.ro

The wide range of drugs discovered, synthesized and marketed that contain pyridin/benzimidazole skeleton demonstrates their applicability in the pharmaceutical and medical field. The antimicrobial and anticancer activity of these compounds stands out[1-3].

Considering the above mentioned, our main goal was to synthesize, characterize and testing of antimicrobial properties of hybrid pyridin-benzimidazole quaternary salts. Using a Bruker Avance III 500 spectrometer equipped with a 5 mm PABBO detection probe, operating at 500.1 MHz for ^{1}H and 125 MHz for ^{13}C, the structures of newly quaternary salts were proved by NMR experiments.

The *in vitro* antimicrobial activity of hybrid quaternary salts was determined by the method Kirby-Bauer disk diffusion, using nutrient agar medium. The strain bacteria used for the antimicrobial activity are illustrated in the figure.



Acknowledgements. This work was supported by a grant of the Romanian Ministry of Education and Research, CNCS-UEFISCDI, project number PN-III-P4-ID-PCE-2020-0371, within PNCDI III. We also thank to CERNESIM Research Centre from ”Al.I. Cuza” University of Iasi, for the NMR experiments.

References:

1.Antoci, V.; Cucu, D.; Zbancioc, Ghe.; Moldoveanu, C.; Mangalagiu, V.; Amăriucăi-Mantu, D.; Aricu, A.; Mangalagiu, I.I. Bis-(imidazole/benzimidazole)-pyridine derivatives: synthesis, structure and antimycobacterial activity. Part XII. Future Medicinal Chemistry (Future Med. Chem.), 2020, 12(3), pp. 207-222. DOI: 10.4155/fmc-2019-0063

2.Lungu, C.N.; Bratanovici, B.I.; Grigore, M.M.; Antoci, V.; Mangalagiu, I.I. Hybrid imidazole-pyridine derivatives: an approach to novel anticancer DNA intercalators. Curr. Med. Chem. 2020, 27(1), pp. 154-169. DOI: https://doi.org/10.2174/0929867326666181220094229

3.Mantu, D.; Antoci, V.; Moldoveanu, C.; Zbancioc, Ghe.; Mangalagiu, I.I. Hybrid imidazole (benzimidazole)/pyridine (quinoline) derivatives and evaluation of their anticancer and antimycobacterial activity. J. Enzym. Inhib. Med. Ch. 2016, 31(sup 2), pp. 96-103. DOI: https://doi.org/10.1080/14756366.2016.1190711

Cost-effective pencil graphite electrode for fast analysis of riboflavin and pyridoxine in pharmaceuticals

Nicoleta Ana-Maria Codreanu, Adrian Popa, Dana Elena Popa, Mihaela Buleandră

University of Bucharest, Faculty of Chemistry, Department of Analytical Chemistry, 4-12 Regina Elisabeta Av., 030018, Bucharest-3, Romania

Water-soluble vitamins, riboflavin (vitamin B_2, VB_2) and pyridoxine (vitamin B_6, VB_6) are essential compounds for normal human growth, many diseases being related to their deficiency. Since they are not synthetized in the organism, they are assimilated from food and dietary supplements. Thus, the development of efficient methods for VB_2 and VB_6 determination in these type o samples is of great interest. Conventional methods are generally based on chromatography, but the voltammetric methods represent a reliable choice to more complex techniques due to their simplicity, low cost and high speed. Despite the fact there are many voltammetric methods for individual determination of B vitamins, only a few approaches were proposed for the analysis of mixtures of two or three different vitamins.

A rapid square wave voltammetric (SWV) method for the simultaneous determination of VB_2 and VB_6 using a pencil graphite electrode (PGE) is reported. This type of electrode is a viable alternative for the modified electrodes. Also, it is disposable electrode, avoiding the time-consuming step of solid electrodes surface cleaning. SWV results in Britton Robinson buffer (BRB) (pH 3) showed distinct anodic peaks at –0.19 V and +1.07 V for VB_2 and VB_6, respectively. Linear relationships between peak currents and vitamin concentrations were obtained from $1 \cdot 10^{-6}$ M to $1 \cdot 10^{-4}$ M for VB_2 and between $1 \cdot 10^{-5}$ M and $1 \cdot 10^{-3}$ M for VB_6. The detection limits were $6.99 \cdot 10^{-7}$ M and $3.42 \cdot 10^{-6}$ M for VB_2 and VB_6, respectively. The SWV method was applied with good recoveries for the quantitative determination of the mentioned compounds in pharmaceutical formulations.

Study of the binary mixtures nimesulide-salicylic acid

Georgescu Mona, **Viorica Meltzer, Elena Pincu**

Faculty of Chemistry, University of Bucharest, Regina Elisabeta Boulevard
No. 4-12, Sector 3, Bucharest - 030018 Romania

In this paper, the thermal study of nimesulide–salicilic acid binary mixtures, as well as of the commercially active principles, was performed in two ways: for the physical mixtures and for the recrystallized mixtures from ethanol, on the entire range of molar fractions. Using the data obtained from differential scanning calorimetry, phase diagrams and Tammann diagrams were made to accurately determine the composition of the eutectic mixture. Regarding the binary physical mixture nimesulide–salicylic acid, the maximum value of the melting enthalpy of the eutectic composition was found at the value of the molar fraction of nimesulide equal to 0,4885. The binary mixtures nimesulide–salicylic acid recrystallized from ethanol has a simple eutectic for the range of molar fractions of nimesulide between 0,1 and 0,8 and the maximum value of the enthalpy of melting of the eutectic composition was found at the molar fraction value of nimesulide equal to 0,5025.

Bienzymatic biocatalyst for cascade transformation of monoterpenes

Maria Cristina Ghetu, Madalina Tudorache

University of Bucharest, Blvd Regina Elisabeta 4-12, Bucharest 030018, Romania

Monoterpenes, such as limonene and α-phellandrene, are natural compounds with wide occurrence. Their oxygenated derivates are used as flavor and fragrance products for centuries [1]. Current literature offers many examples of the monoterpenes biotransformations into terpenoids using whole cell catalysis [2]. However, the whole cell biocatalyst comes with some disadvantages, such as: the difficulty of controlling the process (low selectivity), low tolerance of substrate concentration, and high chances of side reactions [3]. Therefore, we propose a bienzymatic cascade route able as valuable solution.

The two-step cascade process consists of monoterpene biotransformation to the corresponding oxy-derivatives. For the first step, peroxy acid of fatty acids is online produced as the oxidation reagent. Lipase enzyme catalysis the oxidation of the fatty acid. The unstable peroxy acid attacks the substrate leading to epoxy-derivatives. In the second step, a hydrolase enzyme opens the epoxydic cycle, and vicinal diol is produced.

We tested the bienzymatic cascade system using lipase – hydrolase enzymes couple for different substrates transformation, eg (R)-(+)-limonene and α-phellandrene. The tests were performed with Novozym®435 (Candida antarctica B lipase immobilized on acrylic support), Novozym®435 in the presence of free hydrolase, and hydrolise@Novozyme®435 biocomposite. Novozym®435 in the presence of free hydrolase (CH55-LEH) allowed to achieve a conversion of 45% (R)-(+)-limonene and a diol yield of 27%. On the other hand, the biocomposite transformed 74% of (R)-(+)-limonene with 39% yield in limonene-1,2-diol. Additionally, the biocomposite offered 47% of α-phellandrene conversion with 31% yield in p-menth-5-ene-1,2-diol. In all the cases, the enantiomeric excess was above 90% for (1S, 2S, 4R)-(+)-limonene-1,2-diol and (1S, 2S, 4R)-p-menth-5-ene-1,2-diol.

In conclusion, the developed bienzymatic system exhibited the an efficient enantio-biotransformation of (R)-(+)-limonene/ α-phellandrene into diol derivatives which find many applications in the industrial field.

References

[1] C. C. C. R. de Carvalho, M. M. R. de Fonseca, *Biotechnol. Adv.* **2006**, *24*, 134.

[2] A. Sales, G. M. Pastore, J. L. Bicas, *Process Biochem.* **2019**, *86*, 25.

[3] K. Faber, *Biotransformations in Organic Chemistry*, Springer, Berlin, 2004.

Cold-active lipase biocatalysts for silymarin valorization

Giulia Roxana Gheorghita[a)], Cristina Purcarea [b)], Madalina Tudorache [a)]

a) *University of Bucharest, Faculty of Chemistry, Department of Organic Chemistry, Biochemistry and Catalysis, 4-12 Regina Elisabeta Blvd., 030016 Bucharest, Romania*
b) *Institute of Biology Bucharest, Romanian Academy, Department of Microbiology, 296 Splaiul Independentei, 060031 Bucharest, Romania*

Silymarin (*Silybum marianum*), a natural mixture of flavonolignans with valuable worldwide-known medicinal properties, is slightly solubile in both organic and aqueous media, thus consisting its drawback on cellular adsorption and bioavailability. Silybins (A and B, 1:1) are one of the most biologically active compounds from silymarin [1]. Structurally, these are responsible for weak acidic properties due to the chromone ring that enables donor-acceptor interactions with basic counterparts. Meanwhile, the presence of polyphenol hydroxyls sustains the ability to form complexes with transitional metal ions, imprinting to the molecule high oxidant activity [2].

In the frame of drug and cosmetic formulations, we propose a biocatalytic cold-active lipase-mediated system for the acylation of silybin A/B, with proper fatty acids or esters to improve the initial liposolubility.

The biocatalyst is founded on the protein material extracellularly produced by a novel *Psychrobacter sp.* extracted from Scarisoara Ice Cave (Romania). The lipolytic effect of the protein material is considered for the catalyzed reaction, as several extracellular putative lipases could be attributed to species draft genome. In this case, a prior structural analysis was conducted through bioinformatic tools and plate screening assays evidenced the existence of lipases outside the cell [3].

To assure a better stability of the cold-active protein material, covalent attachment to nano-/micro-sized magnetic and polymeric resin particles released final biocatalyst (biocomposite).

The relative enzyme activity was evaluated for both free and immobilized biocatalysts, while the immobilization performance was evaluated through FT-IR and SEM techniques. The performance of the biocatalytic system was followed up through HPLC-DAD method and quantified in terms of substrate conversion for silybin esterification.

[1]. A. Di Costanzo et al., MDPI Molecules, 24 (2019), 2155.
[2]. D. Csupor et al., Journal of Pharmaceutical and Biomedical Analysis, 130 (2016), 301-317.
[3]. L. Ramnath et al., Biotechnology Reports (2017), 15:114-124.

Synthesis and coordination behaviour of new N/S/O macrociclic ligands

Ana Hodorogea, **Alexandra Pop**

Supramolecular Organic and Organometallic Chemistry Centre, Chemistry Department, Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, Cluj-Napoca, Romania,

The chemistry of macrocycle ligands having different donor atoms (*eg.*, N/S, S/O, N/S/O) remains an attractive field due to their various applications in biology, medicine, materials science or catalysis.[1] Macrocycles containing nitrogen and/or sulfur donor atoms are of interest as they exhibit high affinities towards heavy transition metal ions (*eg*. Cd, Hg), and their selectivity is readily tunable by altering the composition of the donor atom set and the ring size. Due to their ability to form stable complexes with different transition metals, macrocyclic metal complexes can act as reagents or catalysts in various organic transformations.[2]

Here in, we report the synthesis and structural characterization of new macrocyclic ligands containing N/S and N/S/O donor atoms and several of their late *d* metals complexes (Ag, Zn, Cd, Hg).

The compounds were investigated in solution by multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{19}F, ^{31}P, as appropriate) and mass spectrometry. Their molecular structures were determined by single-crystal X-ray diffraction.

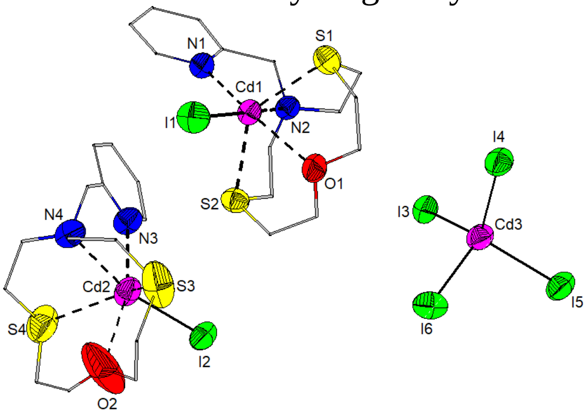


Fig. 1: Solid state structure of the cadmium complex of the 7-(pyridin-2-ylmethyl)-1-oxa-4,10-dithia-7-azacyclododecane ligand.

[1] M. J. Hesford; W. Levason; M. L. Matthews; G. Reid; *Dalton Trans.*, **2003**, 2852-2858.
[2] P. Gull, A. A. Hashmi, *J. Braz. Chem. Soc.*, **2015**, *26(7)*, 1331-1337.

Mesoporous silica - polysaccharide nanocomposites with potential biomedical applications

Simona IONIȚĂ[1], Daniel LINCU[1,2], Mihaela DEACONU[1],
Ana-Maria BREZOIU[1], Raul-Augustin MITRAN[2],
Rodica TATIA[3], Cristian MATEI[1], Daniela BERGER[1]

1 University "Politehnica" of Bucharest, Faculty of Applied Chemistry and Material Science, 1-7 Polizu street, Bucharest, 011061, Romania
2 "Ilie Murgulescu" Institute of Physical Chemistry, Romanian Academy, 202 Splaiul Independentei, Bucharest, 060021, Romania
[3]Departament of Cellular and Molecular Biology, National Institute of R&D for Biological Sciences, 296 Splaiul Independentei, Bucharest 060031, Romania

Lately, seaweeds have received increasing attention because of their composition rich in bioactive compounds that exhibit antibacterial, antioxidant, antiviral and antitumor activity [1]. Some of these bioactive compounds are natural polymers found in their cell walls, such as fucoidan from brown algae and ulvan from green algae. Both ulvan and fucoidan are water soluble polysaccharides that contain a sulphated monosaccharide, *L*-rhamnose-3-sulphate or sulphated fucose, respectively [2].

In this study, ulvan and fucoidan were extracted from green seaweed *Ulva lactuca* and brown seaweed *Ascophyllum Nodosum* (Kelp), respectively. The obtained polysaccharides were used to prepare nanocomposites based on MCM-41 mesoporous silica.

Firstly, the algae were treated to remove the chlorophyll, polyphenols and monosaccharides, and then from the resulted material was Soxhlet extracted polysaccharides-type compounds. The dried polysaccharides, as well as commercial fucoidan were subsequently used to prepare mesoporous silica nanoparticles-polysaccharide nanocomposites with potential biomedical applications. The materials were characterized using various techniques such as FT-IR spectroscopy, scanning electron microscopy, N_2 adsorption/desorption isotherms, thermogravimetric analysis, and X-ray diffraction. The cytotoxicity of the ulvan was assessed on a L929 fibroblast cell line through MTT assay after 24 h and 48 h of incubation and no significant toxic effect was observed up to a concentration of 2 mg/mL extract, suggesting the possibility of the use of nanocomposites in biomedical applications.

References:

1. H. Yaich *et al.*, *Int. J. Biol. Macromol.*, **2017**, 105, 1430-1439.
2. M. Bilal *et al.*, *Mar. Drugs,* **2020**, 18(1), 7.

Voltametric Study of Ferulic Acid

Laura Iordache, **Gabriela Iulia David**

University of Bucharest, Faculty of Chemistry, Department of Analytical Chemistry, 90-92 Panduri Av., 5- Bucharest, Romania

Ferulic acid (FA) was isolated from plants bark or there resin by precipitation with lead in an alcoholic environment and it was re-crystallized from boiling water as free acid [1]. FA is a hydroxi cynamic acid which can be oxidized due to its phenolic groups and therefore it can be studied electrochemically. This paper presents the cyclic voltammetric (CV) behavior of FA on an disposable pencil graphite electrode (PGE) [2] represented by a graphite lead and the development of a differential pulse voltammetry (DPV) method for its rapid and simple quantitative determination.

The influence of the electrode material on the voltammetric response of FA was studied on platinum, glassy carbon electrode, and PGE of different hardness. The most intense signal was obtained for the H-type mine, which was used in the following studies. The electrode surface electroactivation did not enhance the signal. Stability studies indicated that the FA solution electrochemical proprieties changed with time so that the 10^{-2} M FA ethanolic stock solution must to be prepared daily, while the working solutions were stable up to 100 min. Studies regarding the pH influence emphasized that FA peaks involve the same number of H^+ and e^- and the highest signals were obtained in Britton-Robinson buffer with pH 3,00. FA presented a complex voltammetric behaviour (one main oxidation peak and a redox pair in CV). The influence of the scan rate showed that the FA main oxidation peak is due to a diffusion controlled electrode process whereas as the other signals are generated by surface processes. The instrumental parameters of DPV were optimized and the method's linear range was 3 -85 µM FA. The developed DPV method enables the simple, rapid and cost-effective assessment of the total phenolic content of various samples expressed as mg equivalent FA/ mL sample.

References

1. Graf, E. Antioxidant potential of ferrulic acid. Free Radical Biology & Medicine, 1992, 13, 435-448.
2. David, I.G., D. E. Popa, M. Buleandra, Pencil graphite electrodes: a versatile tool in electroanalysis, Journal of Analytical Methods in Chemistry, Volume 2017, Article ID 1905968, 22 pages, 2017.

Influence of microcomponents on the activity of horseradish peroxidase in the oxidation of Coomassie Brilliant Blue G dye with hydrogen peroxide

Delia Mărtinaș, Adina Răducan

University of Bucharest, Faculty of Chemistry, Bulevardul Regina Elisabeta 4-12, Bucharest, 030018, Romania

Horseradish peroxidase (HRP, E.C.1.11.1.7) catalyzes the oxidation of a variety of organic and inorganic compounds and the reduction of peroxides, such as hydrogen peroxide, having a great potential as bioremediation catalyst. The oxidoreductive ability of HRP enzyme has been tested on some model pollutants, such as aromatic amines, dyes and phenolic compounds[1]. In this study we tested the effect of some microcomponents, such as surfactants and transition metals ions often found in wastewater, on the activity of peroxidase in the oxidation of the Coomassie Brilliant Blue G (BB) dye with hydrogen peroxide and sodium bicarbonate. Furthermore, we tested HRP activity in water collected from several lakes and rivers from Romania. The initial rates of reaction in different conditions were estimated from the kinetic curves absorbance vs. time at 619 nm, where the dye has the maximum absorbance.

The experimental data have shown that the HRP activity depends on the surfactant type (anionic, cationic and nonionic); in the presence of the anionic surfactant enzymatic activity decreases, with the nonionic one it remains almost the same, while in the presence of the cationic surfactant the activity of enzyme increases. Regarding the effect of transition metal ions on HRP activity, the results showed that they have an inhibitory effect, except for cobalt ions that activate the enzyme. The results on enzymatic activity in the water samples show that it decreases, but the enzyme remains active in several cycles.

---

[1] Silva, M.C., Torres, J.A., Castro, A.A., da Cunha, E.F.F., et al., Combined experimental and theoretical study on the removal of pollutant compounds by peroxidases: affinity and reactivity toward a bioremediation catalyst. J. Biomol. Struct. Dyn., 34 (2016), 1839:1848.

Hesperidin voltammetric investigation at the pencil graphite electrode

<u>Numan Nimet</u>, David Iulia Gabriela

University of Bucharest, Faculty of Chemistry, Department of Analytical Chemistry, 90-92 Panduri Av., District 5, Bucharest, Romania.

Hesperidin (HESP) is a bioflavonoid mainly found in citrus fruits. It has many beneficial effects on human health like lowering of blood cholesterol, hypotensive and antioxidant effects, being also used for diabetics and gastroesophageal reflux diseases [1]. This work describes (a) the electrochemical behavior of HESP at the disposable pencil graphite electrode (PGE); (b) a differential pulse voltammetric method without (DPV) and with accumulation (AdSDPV) for its quantitative determination and (c) HESP quantification from dietary supplements.

The influence of the electrode material on HESP voltammetric response was tested at Pt, glassy carbon electrode and different PGEs, the most intense signals being obtained at H type PGE. The PGE potentiostatic and potentiodynamic electrochemical activation in various supporting electrolytes did not enhance the HESP anodic peaks. HESP voltammetric behavior was influenced by the solution pH, the highest signal being recorded in Britton Robinson buffer pH 1.81. By increasing the solution pH, the peak potential shifted in the negative direction by a value near to 0.059 V/pH unit, suggesting an equal number of involved electrons and protons.

In the first cyclic voltammetric scan performed in the anodic direction a diffusion controlled oxidation peak was observed at about 0.78 V whereas in the reversed direction a cathodic signal appears 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 the analyte concentration on the currents of HESP oxidation and reduction peaks was investigated by DPV and AdSDPV. The methods showed good linearity with limits of detection of $7.4 \cdot 10^{-8}$ mol·L^{-1} and $1.5 \cdot 10^{-8}$ mol·L^{-1} HESP, respectively. The DPV at PGE method was used for the assessment of the HESP content in dietary supplements. The developed voltammetric methods are rapid, cost-effective and easy to use.

References

[1] D. Srilatha, et al., *ISRN Spectroscopy*, **2013**, *534830*.

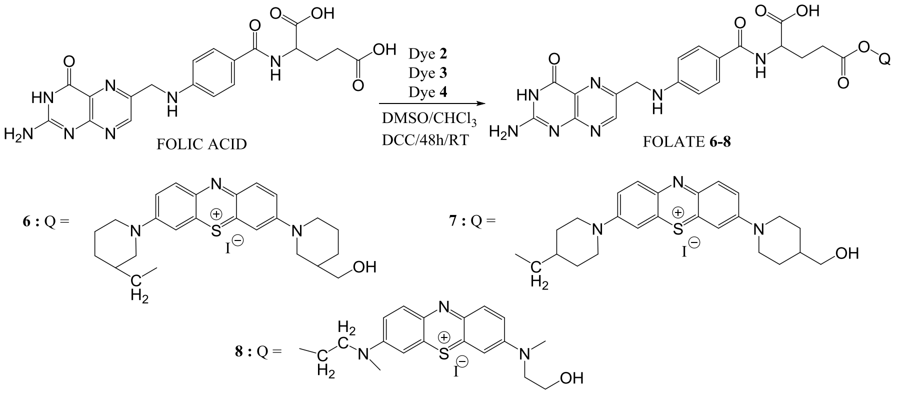
New contrast agents containing methylene blue analogues customized for bioimaging of cancer cells

Bianca-Alexandra Stoean, Castelia Cristea, Luiza Ioana Găină
biancastoean@gmail.com

Research Center on Fundamental and Applied Heterochemistry, Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University, 11 Arany Janos str., RO-400028 Cluj-Napoca, România;

The use of methylene blue 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). [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 and their further use in the preparation of novel folic acid esters (Scheme 1).



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

[1] H. Wada, T. Yamamoto, J. Morimoto, Y. Sakairi, H. Suzuki, T. Nakajima, T. Yoshino, *Ann. Thorac. Surg.*, **2019**, *7*, 10.
[2] S. Bhattacharya, A. Franz, X. Li, B. Jasti, *J. Drug Targeting*, **2008,** *16 (10),* 780.

Structural aspects in mercury complexes with organoselenium ligands

Cătălin Eduard Șalgău and Anca Silvestru

Supramolecular Organic and Organometallic Chemistry Centre, Chemistry Department, Faculty of Chemistry and Chemical Engineering, Babeș-Bolyai University, Cluj-Napoca, Romania

Metal complexes with organochalcogen ligands have attracted an increasing interest due to their potential application in preparing metal chalcogenides by chemical vapour deposition processes. Such compounds are of significant importance as sources for semiconducting materials based on group 12 metal chalcogenides, largely used in technologies producing optoelectronic devices.[1]

In our research group, several group 12 metal (Zn, Cd, Hg) complexes with ligands containing chalcogen donor atoms were synthesized and structurally characterized. A special attention was given to compounds bearing organic groups with pedant arms capable for intramolecular coordination, thus leading to monomeric species, which might behave as single-source precursors for metal chalcogenides.

In the current study, the solution behaviour and the solid-state structure of two mercury organoselenolates, bearing aryl groups with one pedant arm and two pedant arms, respectively, were investigated. The molecular structure of the complex 2-$(Me_2NCH_2)C_6H_4SeHgCl$ (**1**) shows a N→Se coordination, whereas both nitrogen atoms coordinate to selenium in the ionic species [2,6-$(Me_2NCH_2)_2C_6H_3Se][HgCl_3]$ (**2**). In the crystal of compound **1** chain-like polymeric associations are formed, while in the crystal of compound **2** the intermolecular interactions lead to a ribbon-like polymeric structure (Fig. 1).

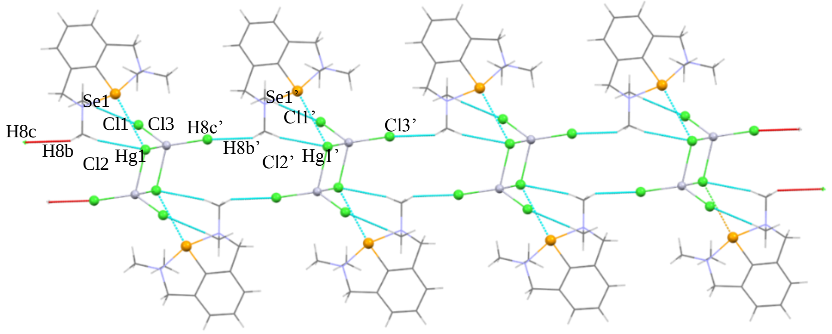


Fig. 1. Ribbon-like polymeric association in the crystal of compound **2**

1. Y. Cheng, T.J. Emge, J.G. Brennan, *Inorg. Chem.*, **1996**, *35*, 342.

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

Paul Adrian Tărăbuță, Cătălin Maxim, Marius Andruh

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], catalysis [2] and pharmacy [3].

Five novel carboxylato Cu^{II} complexes, **1-5**, were obtained from the reactions of three aromatic carboxylic acids with mononuclear precursors.

2-hydroxy-5-methylbenzene-1,3-dicarboxylic acid was synthesized by oxidation of the corresponding bis(hydroxymethyl)phenol and used in the synthesis of mononuclear complex **1**. 1D coordination polymers **2** and **3** are built with benzene-1,3-dicarboxylato spacers (Fig. 1). Dinuclear complexes **4** and **5** were synthesized from pyridine-3-carboxylic acid.

Attempts to synthesize Zn^{II} precursors for carboxylato complexes were made, producing two mononuclear complexes, **I** and **II**. 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. Powder X-ray diffraction and spectroscopic techniques (FTIR and UV-Vis) were also employed for characterization.

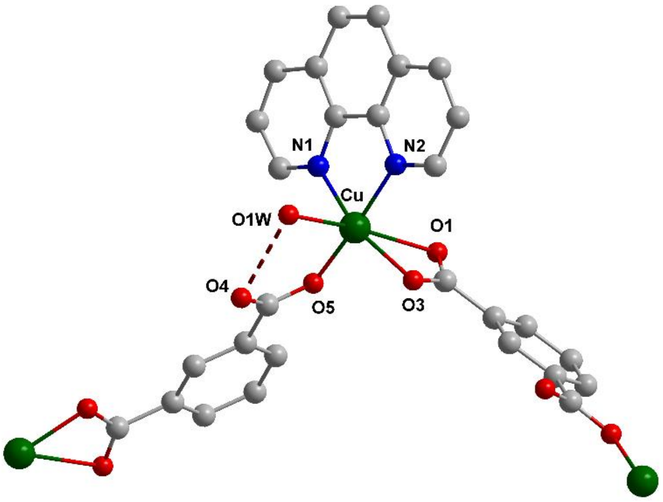


Fig. 1. Crystal structure of coordination polymer **3**.

[1] M. Răducă, et al. *J. Coord. Chem.* **2019**, *72*, 1222.
[2] C. Paraschiv, et al. *Cryst. Growth Des.* **2015**, *15*, 799.
[3] J.Z. Zhang, et al. *Chem. Eur. J.* **2012**, *19*, 1672.

Fabrication of Doped Polyvinyl Alcohol Membranes for Use in Polymer Electrolyte Membrane Fuel Cells

Mihail-Alexandru UDREA[1], Ana-Maria ALBU[1], Cristian-Andi NICOLAE[2]

1-University „Politehnica” of Bucharest, Faculty of Applied Chemistry and Materials Science, Str. Polizu no. 1-7, District 1, 011061, Bucharest, Romania,
2-National Institute for Research & Development in Chemistry and Petrochemistry ICECHIM, Splaiul Independenței no. 202, District 6, Bucharest, Romania

Polymer electrolyte membrane fuel cells (PEMFC) are electrochemical systems that convert chemical energy into electrical energy and have a few advantages such as: low density and intensity DC, they operate without moving parts producing no noise or vibrations, and they lack a liquid electrolyte which may leak in case of mechanical damage. The main objective of this paper was to develop membranes assemblies consisting of polyvinyl alcohol (PVA), acrylic acid, methacrylic acid and in situ generated electrically conductive polyaniline (PANI) and polypyrrole (PPy) which were prepared using the solution casting method. The assemblies were characterized using FT-IR spectroscopy and UV-Vis spectroscopy. The degree of swelling was determined in relation to different solutions over 24 hours.

References

1. Gil-Castell, O., Galindo-Alfaro, D., Sánchez-Ballester, S., Teruel-Juanes, R., Badia, J. D., & Ribes-Greus, A. (2019). Crosslinked sulfonated poly(Vinyl alcohol)/graphene oxide electrospun nanofibers as polyelectrolytes. *Nanomaterials*, *9*(3), 1–20. https://doi.org/10.3390/nano9030397
2. Kim, D. J., Jo, M. J., & Nam, S. Y. (2015). A review of polymer-nanocomposite electrolyte membranes for fuel cell application. *Journal of Industrial and Engineering Chemistry*, *21*, 36–52. https://doi.org/10.1016/j.jiec.2014.04.030

Chelating Macromolecular Architectures with High Ionic Selectivity

Cătălina-Diana UŞURELU[1], Oana Maria MEMECICĂ[1],
Ileana Brândușa RĂU[1], Ana-Maria ALBU[1]

1-University „Politehnica” of Bucharest, Faculty of Applied Chemistry
and Materials Science, 1-7 Gh. Polizu Street, 011061, Bucharest
Romania

The continuous industrial development and on-going use of pesticides and fertilizers in agriculture have led to an increase in the heavy metal ions contamination of *water* and soils. This problem has attracted particular interest since heavy metal ions are toxic, non-biodegradable and they tend to bioaccumulate and biomagnify in the food chains. In the human body, above certain permissible concentrations, they can induce blindness, neurological disorders, cardiovascular diseases, renal damage and gastrointestinal distress, posing serious risks to public health. Some of the most abundant and toxic heavy metal ions are originating from Cr, Ni, Cu, Zn, Cd, Pb, Hg, and As and have their source in the wastewaters resulting from anthropogenic activities such as mining, metal plating, tannery, battery industry, fertilizer and pesticide industries, battery industry etc. In order to protect the environment and the health of the living organisms, the removal of heavy metal ions from water becomes imperative. In the last years, chelating polymeric architectures for heavy metal ions retention have received a special attention, due to their good flexibility, high ionic selectivity, suitable mechanical strength, easy regeneration and the possibility of functionalization with a variety of groups [1].

In this study, we synthesized high-purity poly (maleic anhydride-co-vinylbenzyl chloride) resins for the retention of heavy metal ions from water via the precipitated polymerization techinique. For the obtained resins, retention studies on heavy metal ion solutions of Ni^{2+}, Cu^{2+}, Zn^{2+} and Cr^{3+}, respectively, were performed. For these retention tests, the changes in pH as well as the overall retention yield were discussed in correlation with the compositional/geometric particularities of the support copolymers. In addition, FT-IR analyzes were performed on the chelating polymeric architectures before and after the heavy metal ions retention tests. As perspectives, we want to use the obtained copolymer for the production of ultrafiltration membranes for water purification.

References:

[1]. Fenglian Fu; Qi Wang (2011). Removal of heavy metal ions from wastewaters: A review. , 92(3), 407–418.

Section 3 – PhD Level

The effect of the film thickness on the photoelectrochemical properties of $LaFeO_3$ obtained by pulsed laser deposition

Florin Andrei[1], **Nicu Doinel Scarisoreanu[2]**, **Ioan-Cezar Marcu[1]**

[1]Laboratory of Chemical Technology & Catalysis, Department of Organic Chemistry, Biochemistry & Catalysis, Faculty of Chemistry, University of Bucharest, Blv. Regina Elisabeta, no. 4-12, 030018 Bucharest, Romania.
E-mail: and.florin17@yahoo.com
[2]National Institute for Laser, Plasma and Radiation Physics, Magurele, Romania

Photocatalysis is considered the key of solving energy generation and environmental pollution problems. Perovskites are intensively studied as photocatalysts for several reactions, one of the most important being the generation of hydrogen via photodecomposition of water [1, 2].

In this work, $LaFeO_3$ (LFO) thin films with thicknesses between 10 and 200 nm were prepared by pulsed laser deposition (PLD) technique. PLD is a non-conventional technique, relatively simple and suitable for the production of thin films. LFO thin films exhibit different epitaxial orientations depending on their thickness, and the appearance of self-assembled nanopyramids-like domains beyond a thickness threshold value was proven to have a detrimental effect on the photoelectrochemical (PEC) functional properties. Using Nb:$SrTiO_3$ as conductive substrate and 0.5 M NaOH aqueous solution for PEC measurements, the dependence of the photocurrent density on the physicochemical properties exhibited by the LFO photoelectrodes are unveiled. The potentiodynamic PEC analysis has revealed the highest photocurrent density $J_{photocurrent}$ values (up to 1.2 mA/cm^2) with excellent stability over time, for the thinnest LFO/Nb:$SrTiO_3$ sample. Unbiased hydrogen evolution from water in an aqueous 0.5 M NaOH solution under constant illumination, as determined by gas chromatography, has been evidenced for the LFO thin films.

Acknowledgements

V. Ion, R. Birjega, M. Dinescu, N. Enea, D. Pantelica, A.V. Maraloiu and V.S. Teodorescu are kindly acknowledged for helping us with thin films characterization.

References

1. Rajeshwar, K. Hydrogen generation at irradiated oxide semiconductor–solution interfaces. J. Appl. Electrochem. 2007, 37, 765-787.
2. Wang, W.; Tade, M.O.; Shao, Z. Research progress of perovskite materials in photocatalysis- and photovoltaics-related energy conversion and environmental treatment. Chem. Soc. Rev. 2015, 44, 5371-5408.

Co-crystallization on graphene support

<u>Adrian A. Apostol</u> [1,2], Teodora Mocanu [1,3], Cătălin Maxim [1], Oana Tutunaru [2], Cristina Pachiu [2], Marius Andruh [1]

[1] *University of Bucharest, Faculty of Chemistry, Department of Inorganic Chemistry, Dumbrava Roșie 23, 020464 – Bucharest, Romania*
[2] *National Institute for Research and Development in Microtechnologies, Erou Iancu Nicolae 126A, 077193, Bucharest, Romania*
[3] *"Ilie Murgulescu" Institute of Physical Chemistry, Splaiul Independenței 202, Bucharest, Romania*

Graphene has been intensively studied for its properties, such as very good electrical properties, high mechanical strength or interesting optical properties. Recently, attempts were made to functionalize the graphene surface with different coordination compounds. In order to perform this, the most studied methods are covalent bond formation between support and complex, encapsulation or non-bonding interactions, including hydrogen bonds and π- π stacking. [1,2]

One innovative method to obtain such materials is to perform co-crystallization directly on the surface. For instance, the co-crystallization of azulene-2,2'-bipyridil with *p*-biphenol led to a composite material with uniform dispersion. When the *p*-biphenol is replaced with the brominated derivative (3,3',5,5'-tetrabromo-*p*-biphenol), the resulted material is no longer uniform. Different co-crystals were obtained with this derivative, however none of them give a uniform dispersion on graphene surface. Another promising candidate for a uniform dispersion is the co-crystal from bis(4-pyridyl) mercury and 1,4-diiodotetrafluorobenzene.

All the compounds have been characterized in solid state using FTIR, UV-Vis spectroscopy, powder and single crystal X-ray diffraction. In order to prove that the selected complex has been attached to the graphene, the composite material has been characterized via SEM/EDX and Raman measurements.

[1] K. Karami, A. Ramezanpour, M. Zakariazadeh, C. Silvestru, *Appl. Organometal. Chem.*, **2019**, *33*, e4907.

[2] A. Apostol, I. Mihalache, T. Mocanu, O. Tutunaru, C. Pachiu, R. Gavrilă, C. Maxim, M. Andruh, *Appl. Organometal. Chem.*, **2021**, *35*, e6126.

Grafting natural lignin with aniline using biocatalytic approach

Sabina Ion[1], Anamaria Hanganu[2], Madalina Tudorache[1] and Vasile I. Parvulescu[1]

[1]Department of Organic Chemistry, Biochemistry and Catalysis, University of Bucharest, Soseaua Panduri 90, sector 5, 050663 Bucharest, Romania
[2]Institute of Organic Chemistry C. D. Nenitescu of Romanian Academy, 202B Spl. Independentei, 060023 Bucharest, Romania

Lignin is one of the most abundant natural polymer with large perspective of industrial applications nowadays. Due to the presence of reactive –OH groups, lignin can be modulated using different processes.

This paper presents a biocatalytic method for grafting lignin (grafting bioprocess) with aniline, leading to an amino-derivatized polymeric product with controlled properties (e.g., conductivity, acidity/basicity, thermostability and amino-functionalization). The grafting bioprocess has been developed in different configurations by varying the source of peroxidase, the enzyme concentration and the type of lignin. The insertion of the amine groups was checked by ^{1}H-NMR technique, where NH protons were detected in the range of 5.01–4.99 ppm. The FTIR spectra collected before and after the grafting bioprocess evidenced as well the lignin modification. Additionally, the grafted lignin was characterized using conductivity measurements, gel permeation chromatography (GPC), thermogravimetric analysis (TGA), temperature-programmed desorption (TPD-NH_3/CO_2) and scanning electron microscopy (SEM) analyses. Very important to notice, the resulted grafted lignins exhibit suitable characteristics for industrial applications, such as ion-exchange resins, cationic surfactants, flocculants, coagulants, heavy metal adsorbents or support for protein immobilization.

References:

1. Sabina Ion, Cristina Opris, Bogdan Cojocaru, Madalina Tudorache, Irina Zgura, Aurelian Galca, Adina Bodescu, Madalin Enache, Gabriel Maria, Vasile I Parvulescu, Frontiers in Chemistry, section Green and Environmental Chemistry, April 2018.
2. Lite C, Ion S, Tudorache M, Zgura I, Galca AC, Enache M, Maria G-Mihai, Parvulescu VI, Catalysis Today (2020).
3. **Sabina Gabriela Ion, Teodor Brudiu, Anamaria Hanganu, Florentina Munteanu, Madalin Enache, Gabriel-Mihai Maria, Madalina Tudorache and Vasile Parvulescu, *Molecules* 2020, *25*(21), 4921.**

Temperature dependence of the phase ratio parameter in reversed phase high performance liquid chromatography

Andreia-Cristina Soare, Victor David
University of Bucharest, Faculty of Chemistry, Analytical Chemistry Department, 90-92 Panduri Str., 050663, Bucharest, Romania

Phase ratio, ϕ, for an HPLC column is a parameter defined as the ratio between the volume of the stationary phase, V_{st} and the void volume of the column, V_o. Together with the equilibrium constant of the separation process, K, phase ratio is part of the retention factor k' (k' = K·ϕ). Phase ratio is an important parameter in HPLC being related to the performance of the chromatographic column. One route for the evaluation of the value of ϕ uses the measurements of the retention factors k' on a specific column and mobile phase for two or more hydrocarbons for which the octanol/water partition coefficients log K_{ow} are known [1, 2].

This procedure has been applied in the present study for the evaluation of phase ratio for three commercially available C18 columns and two mobile phase compositions (acetonitrile/water and methanol/water) in the temperature range 20°C to 50°C. It was found that phase ratio does change depending on the temperature [3], its "effective value" decreasing as the temperature increases which is in accordance with the decrease of the retention times in reversed phase HPLC when the temperature increases.

[1] Yun, K. S., Zhu, C., Parcher, J. F., Theoretical relationships between the void volume, mobile phase volume, retention volume, adsorption, and Gibbs free energy in chromatographic processes, *Anal. Chem.*, 67, 1995, 613-619.
[2] Moldoveanu, S., David, V., Estimation of phase ratio in reversed-phase high performance liquid chromatography, *J. Chromatogr. A*, 1381, 2015, 194-201.
[3] Soare, A. C., David, V., Moldoveanu, S. C., Does phase ratio in reversed phase high performance liquid chromatography vary with temperature ?, *J. Chromatogr. A*, 1620, 2020, 461023.

Synthesis and characterization of nitronyl nitroxide metal complexes derived from nitro-*o*-vanillin

Cristian Andrei Spinu[a], **Celine Pichon**[b], **Gabriela Ionita**[c], **Teodora Mocanu**[a,c], **Sergiu Calancea**[a,d], **Mihai Raduca**[a], **Jean-Pascal Sutter**[b], **Mihaela Hillebrand**[e], **Marius Andruh**[a]

[a]*University of Bucharest, Faculty of Chemistry, Inorganic Chemistry Department, Dumbrava Rosie 23, Bucharest 020462, Romania;* [b]*Laboratoire de Chimie de Coordination du CNRS (LCC), Universite de Toulouse, CNRS, Toulouse, France;* [c]*"Ilie Murgulescu" Institute of Physical Chemistry, Romanian Academy, Bucharest, Romania;* [d]*Faculty of Chemistry and Chemical Technology, Moldova State University, Chisinau, Moldova;* [e]*Physical Chemistry Department, Faculty of Chemistry, University of Bucharest, Bucharest, Romania*

Heterospin complexes with spin carriers of different nature can be synthesized using stable and persistent organic radicals[1] and metal ions.[2]

In this work we investigated the coordination ability of a nitronyl nitroxide[3] organic radical, derived from nitro-*o*-vanillin, as a ligand towards 3d[4] and 4f metal ions. The structures of the newly synthesized compounds have been solved by single-crystal diffraction studies, and their cryomagnetic as well as their spectral properties have been investigated.

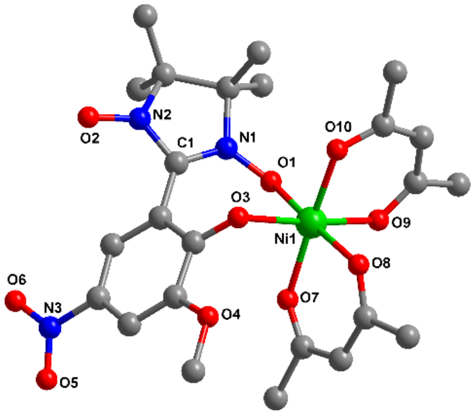


Figure 1. Molecular structure of $[\mathrm{NiL(hfac)_2}]^-$ anion.

[1] R. G. Hicks, Stable Radicals: Fundamentals and Applied Aspects of Odd-Electron Compounds, **2010**, John Wiley & Sons Ltd.

[2] M. G. F. Vaz, M. Andruh, *Coord. Chem. Rev.*, **2021**, *427*, 213611.

[3] J. H. Osiecki, E. F. Ullman, *J. Am. Chem. Soc.*, **1968**, *90*, 4, 1078-1079.

[4] C. A. Spinu, C. Pichon, G. Ionita, T. Mocanu, S. Calancea, M. Raduca, J.-P. Sutter, M. Hillebrand, M. Andruh, *J. Coord. Chem.*, **2021**, *74*, 1-3, 279-293.

Synthesis, characterization and catalytic activity of $Mg_3Al_{0.75}Ce_{0.25}$-LDH-GO composites

Alexandra-Elisabeta Stamate, Rodica Zăvoianu, Octavian Dumitru Pavel, Ioan-Cezar Marcu
University of Bucharest, Faculty of Chemistry, Dept. of Organic Chemistry, Biochemistry & Catalysis, Bd. Regina Elisabeta no. 4-12, Bucharest, 030018, Romania

A topical subject that nowadays intrigues the field of catalysis is the synthesis of new hybrid composites based on the synergistic effect of different nano-metric compounds [1]. The combination of layered double hydroxides (LDH) with components such as graphene oxide (GO), a 2D honeycomb material with appreciable oxidizing properties [2] can endow the formation of nanohybrids with multiple, improved properties that will definitely bring great contributions to many fields of application [1].

The current study focuses on the structural and catalytic properties of $Mg_3Al_{0.75}Ce_{0.25}$ LDH-GO composites bearing different concentrations of GO in the range of 5-15 wt. % abbreviated as HT3Ce-xGO where *x* stands for the concentration of GO (*x* = 5, 10, 15 wt. %). The synthesis of the composites was performed by co-precipitating the LDH phase in the presence of a GO suspension, while their characterization was performed using XRD, DRIFT, and SEM.

Their catalytic activity was studied in the Knoevenagel condensation reaction of benzaldehyde with diethylmalonate in a glass batch reactor, under reflux, stirred and heated at 160 ˚C in a silicon oil bath, for 5 hours. The HT3Ce-*x*GO composites showed catalytic performances in strong contrast to neat HT3Ce or GO (with no activity). Moreover, during Knoevenagel condensation reactions, the catalytic activity increased with the GO content in the hybrids, indicating a better accessibility of the reactants to the base sites.

Acknowledgements
This work was supported by a grant of the Romanian Ministry of Research and Innovation, CCCDI - UEFISCDI, project number PN-III-P1-1.2-PCCDI-2017-0387/80PCCDI Acronym EMERG2Ind, within PNCDIII

References

1. Lonkar, S.P., Raquez, J.M., Dubois, P. One-Pot Microwave-Assisted Synthesis of Graphene/Layered Double Hydroxide (LDH) Nanohybrids, Nano-Micro Lett. 2015, 7, 332–340.

2. Dreyer, D.R., Jia, H.P., Bielawski, C.W. Graphene Oxide: A Convenient Carbocatalyst for Facilitating Oxidation and Hydration Reactions, Angew. Chem. Int. Ed. 2010, 49, 6813 –6816.

The effect of Co content on the catalytic performance of Co(x)-CeMgAlO ex-LDH mixed oxides in methane total oxidation

Marius C. Stoian[1], **Ionel Popescu**[2], **Ioan-Cezar Marcu**[1,2]

[1]Laboratory of Chemical Technology and Catalysis, Department of Organic Chemistry, Biochemistry and Catalysis, Faculty of Chemistry, University of Bucharest, 4 - 12, Blv. Regina Elisabeta, 030018, Bucharest, Romania. marius7stoian@gmail.com
[2]Research Center for Catalysts and Catalytic Processes, Faculty of Chemistry, University of Bucharest, 4 - 12, Blv. Regina Elisabeta, 030018, Bucharest, Romania

Catalytic combustion represents the most effective process for volatile organic compounds (VOC) destruction, to limit their release in the atmosphere[1]. Transition-metal-based mixed oxides derived from layered double hydroxides (LDH) precursors have displayed great activity in VOC catalytic combustion[2].

This work studies the effect of Co content in a series of LDH-derived Co(x)-CeMgAlO mixed oxides with x = 7, 14, 21, 30, 40 and 50 at.% Co, 10 at.% Ce (at.% with respect to cations) and Mg/Al atomic ratio of 3, on their catalytic performance in the combustion of methane as VOC test molecule. Characterized by XRD, EDX, XPS, TPR and TPO, the catalytic materials showed activity in methane total oxidation tests (1 vol.% CH_4 in air and VHSV of 16,000 h^{-1}), strongly dependent on the Co content. Thus, the temperature corresponding to 50 % methane conversion (T_{50}) decreases with increasing the Co content, passing through a minimum for the Co(40) sample. Its highest Co/Ce surface atomic ratio determined from XPS analysis together with its enhanced redox behavior revealed by TPR/TPO measurements explain the increased activity of the Co(40)-CeMgAlO system.

Acknowledgements

C. Romanițan, G. Crăciun, D. Culiță, F. Papa and C. Negrilă are kindly acknowledged for helping us with catalysts characterization.

References

1. P. Kuśtrowski, A. Rokicińska, T. Kondratowicz, *Adv. Inorg. Chem.* 2018, 72, 385-419.
2. I.-C. Marcu, A. Urdă, I. Popescu, V. Hulea, Layered Double Hydroxides-based Materials as Oxidation Catalysts, in *Sustainable Nanosystems Development, Properties and Applications* (Putz, M.V., Mirica M.C., Eds.), IGI Global, Hershey, PA, USA, 2017, Ch. 3, pp. 59-121.

Luminescence thermometry based on 1D benzoato-bridged coordination polymers containing lanthanide ions

<u>Alexandru Topor</u>,[a] Daniel Avram,[b] Catalin Maxim,[a] Carmen Tiseanu,[b] Marius Andruh[a]

[a]University of Bucharest, Faculty of Chemistry, Inorganic Chemistry Laboratory, Str. Dumbrava Rosie nr. 23, 020464-Bucharest, Romania
[b]National Institute for Laser, Plasma and Radiation Physics, RO, 76900, Bucharest-Magurele, Romania

Lanthanide compounds have recently found interesting applications for thermometry, including cryogenic temperatures. As opposed to traditional contact thermometers, which require heat transfer and thermal equilibrium, non-contact thermometry is accurate, non-invasive and allows measurements for moving objects or inside cells.[1]

We report on three new lanthanide benzoato-bridged 1D-coordination polymers, their photophysical properties have been investigated, with special emphasis on ratiometric thermometry studies of a Tb/Eu system using time-gated luminescence detection,[2] employed on this type of system for the first time, which allows us to reduce the spectral overlap of Tb^{III} and Eu^{III} emissions. In addition, these compounds also show X-ray induced visible luminescence, and thus have potential applications as scintillating materials.[3]

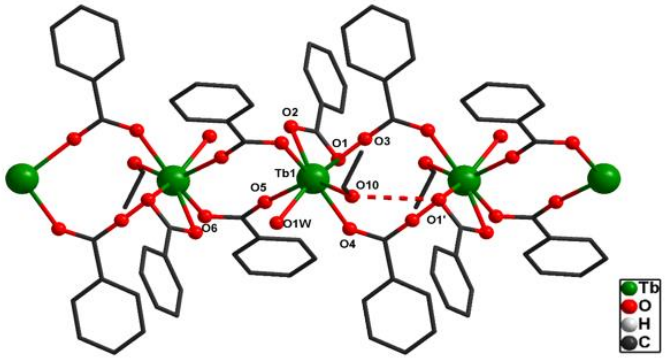


Fig 1. Molecular structure of $^{1}_{\infty}[Tb(PhCOO)_3(H_2O)(EtOH)]\cdot 0.5(18C6)$

1. X.-D. Wang, O. S. Wolfbeis, R. J. Meier, *Chem. Soc. Rev.*, 2013, **42**, 7834.
2. D. Avram, M. Sanchez-Dominguez, B. Cojocaru, M. Florea, V. Parvulescu, C. Tiseanu, *J. Phys. Chem. C.*, 2015, **119**(28), 16303.
3. A. A. Kukinov, T. V. Balashova, V. A. Ilichev, A. N. Trufanov, M. N. Ivin, S. V. Obolensky, M. N. Bochkarev, *Phys. Chem. Chem. Phys.*, 2019, **21**, 16288.