

PROGRAM

Zilele Academice Clujene - 2021

- secțiunea CHIMIE -

Perioada: 21-22 octombrie 2021

Locul de desfășurare: Facultatea de Chimie și Inginerie Chimică
Str. Arany Janos 11
online – ZOOM

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Meeting ID: 488 619 9936

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Joi, 21 octombrie 2021

9:40-10:00

Cuvânt de deschidere

Acad. Cristian SILVESTRU

Prof. Daniel DAVID, Rectorul Universității Babeș-Bolyai din Cluj-Napoca

Acad. Marius ANDRUH, Președintele Secției de Științe Chimice a Academiei Române

Prof. Gabriela NEMEŞ, Decanul Facultății de Chimie și Inginerie Chimică

Chairman: **Acad. Marius ANDRUH**

10:00-10:40

Catalysis in the circular economy concept

Prof. Vasile I. PÂRVULESCU

Center of Catalysts and Catalysis Processes, University of Bucharest, Bucharest,
Romania

10:40-11:20

CO₂ transformation in value-added compounds catalyzed by oxide supported Ni materials with controlled porosity

CS I Dr. Mihaela Diana LAZĂR

National Institute for R&D of Isotopic and Molecular Technologies – INCDTIM,
Cluj-Napoca, Romania

11:20-11:30 Pauză de cafea

Zilele Academice Clujene - 2021

Chairman: **Prof. Gabriela NEMEŞ**

11:30-12:10

The need and possibility to determine the chemical vapor generating elements by spectral methods without derivatization - applicability of microplasma sources to environmental and food samples

Prof. Tiberiu FRENTIU

Department of Chemistry, Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University, Cluj-Napoca, Romania

12:10-12:30

Determinarea unor elemente din deşeuri de plastic şi baterii pe bază de plumb utilizând spectrometria de emisie optică în microplasmă cuplată capacitiv şi vaporizare electrotermică

Drd. Simion Bogdan ANGYUS

Departamentul de Chimie, Facultatea de Chimie şi Inginerie Chimică, Universitatea Babeş-Bolyai, Cluj-Napoca, România, şi

Institutul de Cercetare pentru Instrumentaţie Analitică din Cluj-Napoca, filială a Institutului Naţional de Cercetare – Dezvoltare pentru Optoelectronică - INCD INOE 2000, Bucureşti, România

12:30-12:50

Dezvoltarea şi evaluarea unei metode de determinare a arsenului total şi anorganic în probe de mediu, alimentare şi materiale prin generare de hidruri şi detecţie prin spectrometria de absorbiţie atomică de înaltă rezoluţie cu sursă continuă

Drd. Lucia CHIRIȚA

Departamentul de Chimie, Facultatea de Chimie şi Inginerie Chimică, Universitatea Babeş-Bolyai, Cluj-Napoca, România

12:50-15:00 Pauză de masă

Chairman: **Prof. Anca SILVESTRU**

15:00-15:40

Non-covalent interactions – useful tools in crystal engineering

Acad. Marius ANDRUH

Departamentul de Chimie Anorganică, Facultatea de Chimie, Universitatea din Bucureşti, Bucureşti, România

15:40-16:20

Beyond the Wade-Mingos rules: deviations from sphericity in metallaborane structures

Conf. Dr. Alexandru LUPAN

Departamentul de Inginerie Chimică, Facultatea de Chimie şi Inginerie Chimică, Universitatea Babeş-Bolyai, Cluj-Napoca, România

16:20-16:40

Nanoparticule metalice cu activitate biologică

Conf. Dr. Luminiţa DAVID

Departamentul de Chimie, Facultatea de Chimie şi Inginerie Chimică, Universitatea Babeş-Bolyai, Cluj-Napoca, România

16:40-17:00

Compuși staniu(IV)-organici polimetalici

Conf. Dr. Richard A. VARGA

Centrul de Chimie Supramoleculară Organică și Organometalică, Departamentul de Chimie, Facultatea de Chimie și Inginerie Chimică, Universitatea Babeș-Bolyai, Cluj-Napoca, România

17:00-17:20

Sinteza și reactivitatea unor noi derivați fosfaalchenilici de tipul P=C-P=Y

Lect. Dr. Raluca ȘEPTELEAN

Departamentul de Chimie, Facultatea de Chimie și Inginerie Chimică, Universitatea Babeș-Bolyai, Cluj-Napoca, România

17:20-17:40

Pincer ligands in p-block chemistry

Lect. Dr. Noémi DEAK

Department of Chemistry and Chemical Engineering - Hungarian Line of Study, Faculty of Chemistry and Chemical Engineering, Babeș-Bolyai University, Cluj-Napoca, Romania

Vineri, 22 octombrie 2021

Chairman: **Acad. Cristian SILVESTRU**

10:00-10:40

Low coordinate main group metal complexes: Synthetic challenges and reactivity opportunities

Dr. Yann SARAZIN

Institut des Sciences Chimiques de Rennes - UMR 6226 CNRS, Université de Rennes 1, Rennes, France, and

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

10:40-11:20

Poly(2-isopropenyl-2-oxazoline) – smart polymeric material for advanced applications

CSII Dr. Valentin Victor JERCA

Centre of Organic Chemistry “Costin D. Nenitzescu”, Romanian Academy, Bucharest, Romania

11:20-11:30 Pauză de cafea

Chairman: **Prof. Tiberiu FRENTIU**

11:30-12:10

Organometallic compounds of heavy pnicogens. Synthesis, structure and catalytical applications

Prof. Anca SILVESTRU

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

12:10-12:30

Novel diorganotin(IV) and diorganolead(IV) complexes containing tetraphenyldichalcogenoimidodiphosphinato ligands

Drd. Eleonóra KAPRONCZAI

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

12:30-12:50

Silver complexes with diorganochalcogen ligands of type (2-XC₆H₄CH₂)₂E (E = S, Se; X = Br, CH₃)

Drd. Anamaria Lavinia CORJUC

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

12:50-13:10

Novel silver(I) complexes of organoselenium ligands bearing organic groups with pendant arms and pyrazole or phenylthiazole moieties

Drd. Roxana A. POPA

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

13:10-13:30

Diorganoselenides and their late d-metal complexes. Synthesis and structural characterization

MSc. Stud. Maria DAVID

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

13:30

Cuvânt de închidere

Acad. Cristian SILVESTRU

Catalysis in the circular economy concept

Vasile I. PÂRVULESCU

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Circular economy (also referred to as "circularity") defines an economic system that tackles global challenges like climate change, biodiversity loss, wastes, and pollution. Chemistry is playing an important role in this system since most of the challenges have it at the origin. To limit the negative effects Circular economy operates with a series of concepts such as: reuse, share, repair, refurbish or remanufacture (Figure 1) [2]. Therefore, its application is expected to eliminate wastes and regenerate natural systems.

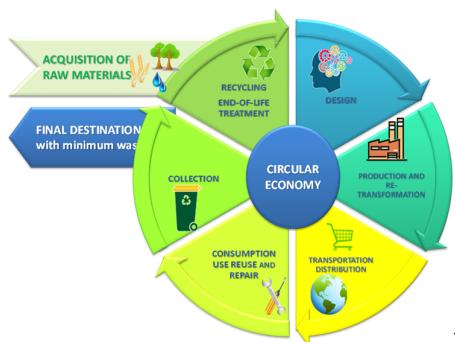


Figure 1. Visualization of the Circular economy concept

Recycling of valuable resources represents a mandatory key instrument of the moments. Catalysis is at “the heart” of the efficient transformations of the molecules and materials and on this basis is a needed important actor for a **circular economy** [3]. Recycling food, agriculture, textile, plastics and carbon dioxide wastes can be efficiently achieved only utilizing catalysis.

To date, reports indicate the use of catalysis in such processes in both the homogeneous catalysis (catalysis with metal complexes and biocatalysis) and biphasic systems (heterogeneous catalysis and photocatalysis). However, heterogeneous catalysis is more preferred due to the possibility to recover catalysts also affording a complete sustainability of catalysts containing expensive metals. This makes even more sense where the catalysts are as well prepared from renewable wastes and can be recycled. Based on this state of the art, in line with the circular economy concepts, this contribution will focus three aspects: i) heterogeneous catalysts from wastes and their efficiency; ii) heterogeneous catalysis in valorization of water soluble biowastes and iii) valorization of CO₂ following the Circular economy concepts.

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CO₂ transformation in value-added compounds catalyzed by oxide supported Ni materials with controlled porosity

Mihaela Diana LAZĂR

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Globally, there is an acute “wake-up call” to reduce the CO₂ emissions in order to prevent its increasing atmospheric concentration. As CO₂ capture and storage concept starts to show its limits, the idea of CO₂ capture and utilization becomes more and more attractive. Two possibilities of CO₂ valorization will be approached in this presentation: (i) CO₂ methanation and (ii) syngas production by combined CO₂ and steam reforming of methane. Both processes need active and selective catalysts to be efficient. New alumina and silica supported materials with Ni as active phase, lanthanum and cerium oxides as promoters and designed porous structure were prepared, characterized and tested in both reactions. All materials presented bimodal porous structure with larger pores size at least double compared to smaller pores for one specific sample. The larger pores have the dimensions between 17 and 36 nm while the smaller ones between 8 and 16 nm. The results showed that the best catalytic activity for both processes was obtained for lanthana containing catalysts due to the cumulative effects of: (i) improved capacity to activate both hydrogen and carbon dioxide, (ii) the combined effect of Ni nanoparticles stabilization inside the small mesopores, and the facilitated access of reagents to active centers due to the large mesopores.

The need and possibility to determine the chemical vapor generating elements by spectral methods without derivatization - applicability of microplasma sources to environmental and food samples

Tiberiu FRENTIU

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The simultaneous determination of chemical vapor generating elements by spectral methods continues to be a challenge in the scientific community of analytical chemists. The need to determine these elements in various matrices is motivated by extremely high toxicity, such as that of Hg and Pb classified as priority dangerous elements and the first category of carcinogenic elements with a disastrous effect on the nervous system. The determination of these elements usually involves *on-line* derivatization with the detection method in order to improve the detection limits, but this approach limits the simultaneous determination, due to the different conditions in the pre-reduction and derivatization stage. The common detection methods are based on inductively coupled plasma optical emission spectrometry and mass spectrometry (ICP-OES and ICP-MS) and atomic absorption spectrometry. Although the ICP-OES and ICP-MS methods are simultaneous, they are difficult to access due to the high purchase price, the atomic absorption method is a slow sequential one with high sample and reagent consumption. Therefore, microplasmas technology and their applications is a critical approach in green atomic spectrometry. The applicability of microplasmas continues to be limited in the case of liquid sample analysis due to low operating power and limited excitation capacity. A new direct liquid microsampling method for the simultaneous determination of As, Bi, Se, Te, Hg, Pb, Sn in cave and river sediment samples and mercury speciation in food and river sediment, using a fully miniaturized set-up based on small-sized electrothermal vaporization and low-power (15 W) and low Ar consumption (150 ml min^{-1}) capacitively coupled plasma microtorch optical emission spectrometry, interfaced with a low-resolution microspectrometer (0.35 - 0.4 nm) was developed. The characteristics of the emission spectrum and the figures of merit were studied in detail. The green degree of the new methods on the eco-analytical scale is 70%, almost excellent (over 75%).

Acknowledgements

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Non-covalent interactions – useful tools in crystal engineering

Marius ANDRUH

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The search for crystalline molecular materials showing interesting and technologically useful properties is one of the most important challenges of crystal engineering. All the synthetic approaches leading to such systems rely on the directionality of the interactions connecting the building-blocks. Apart from the coordination bonds, largely employed to construct molecular solids, other interactions can be useful too: hydrogen and halogen bonds (both directional), metallophilic and π - π stacking interactions. Having in mind that “the crystal is a supramolecular entity” (G. R. Desiraju), we currently design new solid-state architectures resulting from the convolution of coordinative and non-covalent interactions. A special emphasis is given to systems containing two different metal ions, as well as to co-crystallization processes.

Beyond the Wade-Mingos Rules: deviations from sphericity in metallaborane structures

**Alexandru LUPAN, Amr A. ATTIA, Szabolcs JÁKÓ, Attila Zs. KUN
and R. Bruce KING**

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Metallaboranes and metallacarboranes can exhibit deviations from the closo deltahedral geometries because of the energetic preference of transition metals for higher degree vertices as compared to boron or carbon. Isocloso structures with a metal atom located at a degree six vertex and having two fewer skeletal electrons as compared to the closo structures represent a minor deviation from the sphericity and favorable especially for the 10 vertex systems. More significant deviations from sphericity are encountered for the oblate ellipsoidal dirhenaborane structures having the rhenium atoms located antipodally at degree 6 and 7 vertices with a lower deltahedral surface curvature as compared to the boron atoms which are situated at degree 4 or 5 vertices. Theoretical predictions on isoelectronic species such as the dichromadicarbaboranes suggest a structure with a surface chromium-chromium triple bond bridged by two hydrogen atoms.

Low coordinate main group metal complexes: Synthetic challenges and reactivity opportunities

Yann SARAZIN

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This lecture will present some recent insight in the burgeoning molecular chemistry of the heavy alkaline-earths metals calcium, strontium and barium. The design of low-coordinate complexes - in particular alkaline-earth tetrelides and alkoxo derivatives - will be broadly discussed along their main structural and bonding properties. The implementation of these well-defined complexes in homogeneous catalysis will be illustrated through the construction of E-E' bond between heteroelements during alkaline-earth-catalysed dehydrogenative coupling reactions, e.g. for the controlled and atom-efficient creation of silazane or borasiloxane materials.

Poly(2-isopropenyl-2-oxazoline) – smart polymeric material for advanced applications

Valentin Victor JERCA

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Multifunctional materials are designed to meet specific requirements through tailored properties. Nowadays, there is a high demand for “smart” materials with integrated functionalities that make them responsive to multiple stimuli, switchable and adaptive. “Smart” or stimuli-responsive materials can alter their chemical and/or physical properties upon exposure to external stimuli.¹ The development of specialized stimuli-responsive polymers with potential applications in harvesting the photomechanical energy, healable hard coatings, self-repellent surfaces, detecting and sensing is witnessing exciting progress.² However, designing accessible stimuli-responsive polymers that can function as multi-signal processing sensors is of particular interest. Inspired by this promising progress and current interest, we envisioned that poly(2-isopropenyl-2-oxazoline) (PiPOx) can stand as a reactive functional platform for the synthesis of well-defined stimuli-responsive materials.

The polymerization of iPOx has been reported in early 1970s. However, this polymer was almost forgotten due to the controversies related to its polymerization conditions and limited application possibilities. In the last decade, a revival of PiPOx has arisen because of its potential use in the field of stimuli responsive materials and biomaterials^{3,4}, as well as the easy access to a wide variety of structures with defined and controlled properties via post-polymerization modification reactions with (di)carboxylic acids.⁵⁻⁷ The versatility of this modification method allows the synthesis of a wide variety of functional polymers with tunable properties from soft to hard materials.⁸⁻¹⁰

Recent developments from our research group that illustrate the potential of PiPOx as smart (bio)materials will be discussed in this lecture, ranging from fundamental studies on ring opening addition of PiPOx with carboxylic acids to emerging applications of these polymers as temperature sensors,⁵ ophthalmologic biomaterials⁴, materials for detection and sensing applications, drug delivery vehicles⁸, though hydrogels⁹, and materials for water purification¹⁰.

Acknowledgements

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Organometallic compounds of heavy pnicogens. Synthesis, structure and catalytical applications

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The tremendous development in organic synthesis is strongly related to the continuous search for efficient catalytic systems with high selectivity, capable to reduce the reaction time and the effective costs of the processes. Nowadays constant efforts are made to replace the catalysts based on costly transition metals with species containing main group metals. In this way not only the costs are reduced, but also the contamination of the final products and the toxicity of the associated processes. Moreover, *green conditions* of synthesis can be easily employed in catalytic processes with main group metal based catalysts.[1]

In this context, hypercoordinated organopnicogen (Sb, Bi) compounds became very attractive in the last years due to their increased hydrolytic and thermal stability and their valuable applications in organic synthesis. Organoantimony and -bismuth compounds with intramolecular N→M coordination were reported as efficient agents for various organic transformations,[2] or were described as efficient reagents for reversible CO₂ fixation.[3,4]

During last years our research interest included hypercoordinated diorganopnicogen(III) compounds and we report here about several new derivatives with N→M or E→M (M = Sb, Bi; E = N, O) intramolecular interactions, bearing either 2-(Me₂NCH₂)C₆H₄, E(CH₂C₆H₄)₂ or RCH₂N(CH₂C₆H₄)₂ (R = Ph, Bn, CH₂OMe) organic groups. For selected species the catalytic behaviour is also discussed.

Acknowledgements

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Determinarea unor elemente din deșeuri de plastic și baterii pe bază de plumb utilizând spectrometria de emisie optică în microplasmă cuplată capacativ și vaporizare electrotermică

Simion Bogdan ANGYUS^{1,2}, Tiberiu FRENTIU¹

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Scopul acestui studiu a fost evaluarea performanțelor analitice a unui spectrometru cu emisie optică în microplasmă cuplată capacativ și vaporizare electrotermică (SSETV- μ CCP-OES) pentru determinarea simultană a unor elemente cum ar fi S, As, Se, Sb, Bi, Te, Pb, Hg, Zn și Cd din probe de deșeu de plastic și baterii pe bază de plumb. Prezența acestor elemente în masele plastice se datorează aditivilor adăugați pentru îmbunătățirea proprietăților acestora și a coloranților pe bază de săruri de metale [1]. Bateriile pe bază de plumb utilizează aliaje ale plumbului cu diferite metale cum ar fi Sb, Bi sau Sn. Prezența acestor metale în aliajul de plumb îmbunătățesc performanțele bateriilor [2] dar totodată cresc riscul de contaminare al mediului și pot avea efecte dezastroase asupra ecosistemelor dacă deșeurile de baterii nu sunt recuperate corespunzător pentru reciclare [3]. Metoda propusă posedă limite de detecție bune cuprinse între 0.5 $\mu\text{g L}^{-1}$ (Cd), respectiv 15 $\mu\text{g L}^{-1}$ (Bi), o precizie cuprinsă între 1% și 11% și grade de recuperare cuprinse între 91% și 108%

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**Dezvoltarea și evaluarea unei metode de determinare a arsenului total și anorganic
în probe de mediu, alimentare și materiale prin generare de hidruri și detecție prin
spectrometria de absorbție atomică de înaltă rezoluție cu sursă continuă**

Lucia CHIRITA, Tiberiu FRENTIU

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Studiul a avut drept scop dezvoltarea unor metode de determinare a arsenului total (tAs) și anorganic (iAs) din probe de apă, alimente (pește, orez, alimente pentru copii) și mediu (sol, sedimente) folosind generarea la arsină și detecția prin spectrometria de absorbție atomică de înaltă rezoluție cu sursă continuă în cupitor de cuarț (HR-CS-QFAAS). Determinarea tAs se realizează prin mineralizarea a 0,5g probă cu 12 ml apă regală și se aplică o prereducere As(V) la As(III) folosind o soluție de 0,2% L-cisteină în mediu de 0,01 mol l⁻¹ HCl (pH 2,00 ± 0,01). Derivatizarea la hidruri de arsina se realizează folosind soluția de 0,6% (m/v) NaBH₄ stabilizată în 0,01% (m/v) NaOH. Pentru determinarea iAs au fost investigate 2 metode de extracție: (i) în HCl 10 mol l⁻¹ pentru probele de mediu și alimente, cu și fără extracție în toluen și (ii) extracție în HNO₃ 0,28 mol l⁻¹ pentru probele de alimente și prereducerea As(V) la As(III) cu 0,2% L-cisteină în mediu de HCl de 0,01 mol l⁻¹ (pH 2,00 ± 0,01). Cele 2 metode au fost comparate cu metoda recomandată de Autoritatea Europeană pentru Siguranța Alimentară (EFSA) pe baza protocolului IMEP 41 (*Collaborative Trial Report*)¹, care presupune extracția speciilor de iAs în 10 mol l⁻¹ HCl, prereducerea cu 15 g l⁻¹ sulfat de hidrazină în mediu de HBr, urmată de dubla extracție în cloroform. Determinările iAs s-au realizat prin metoda calibrării externe și a adiției standard pentru a studia eventualele efecte spectrale. În urma analizelor efectuate s-a constatat prezența efectelor spectrale provenite de la matricea organică, iar ca urmare este necesar utilizarea metodei de adiție standard, atât în cazul extracției în 10 mol l⁻¹ HCl, cât și în cazul extracției în 0,28 mol l⁻¹ HNO₃. Metodele dezvoltate au fost aplicate pe materiale certificate de referință, obținând un grad de regăsire mediu de 99±10%. Limita detectie obținută în extracte lichide a fost de 0,081 ± 0,008 µg l⁻¹, iar în probe de alimente și de mediu 0,0051 ± 0,0005 mg kg⁻¹ în cazul tAs și 0,0081±0,0004 mg kg⁻¹ în cazul iAs. S-a constat că metoda dezvoltată pentru determinarea tAs este lipsită de interferențe spectrale și non-spectrale, are o sensibilitate mare și poate fi implementată în laboratoare pentru analize de rutină.

Mulțumiri

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Nanoparticule metalice cu activitate biologica

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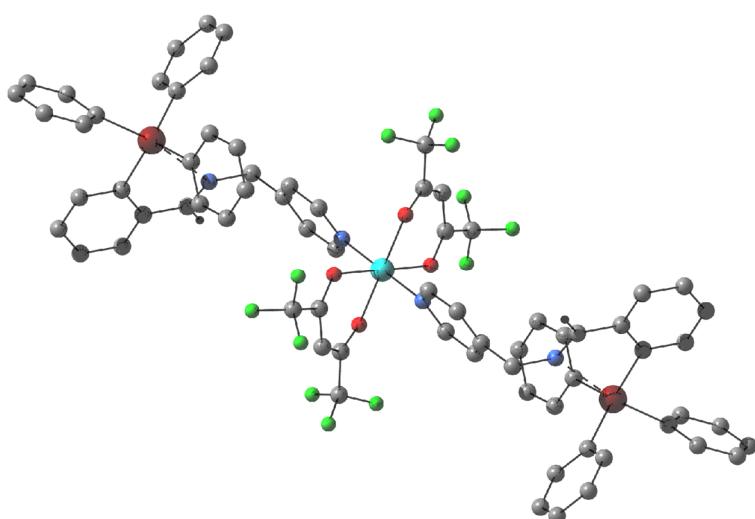
Fructele unor arbuști din flora spontană a României (corn, călin, soc, sănger) au fost utilizate ca surse de agenți reducători pentru obținerea nanoparticulelor metalice de aur și argint prin reducerea ionilor corespunzători, utilizând metode specifice chimiei verzi. Nanoparticulele astfel obținute au fost caracterizate cu ajutorul unor metode fizice consacrate (UV-Vis, FT-IR, TEM, XRD, EDX) fiind totodată investigate din punctul de vedere al proprietăților lor biologice. Studiile au demonstrat că activitatea antiinflamatoare, antitumorală și antidiabetică a acestor nanoparticule metalice le recomandă drept candidați serioși pentru obținerea unor medicamente eficiente în tratamentul cancerului, diabetului și a unor boli de natură inflamatorie.

Compuși staniu(IV)-organici polimetalici

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O serie de compuși staniu(IV)-organici homo- și heteropolimetalici (de exemplu: $\{[2-(1,1'-C_6H_5C_6H_4-4-N=CH)C_6H_4]SnMe_2\}_2S$, $ClSnMe_2[2-C_6H_4(4-CH=N-1,1'-C_6H_4C_6H_4-4'-N=CH)-2'-C_6H_4]Me_2SnCl$, $\{[2-(4'-PyCH_2N=CH_2)C_6H_4SnPh_3\}_2Cu(hfac)_2\}$) au fost sintetizați și investigați atât în soluție prin spectroscopie RMN multinucleară, cât și în stare solidă prin difracție de raze X pe monocristal. Derivații homometalici prezintă fie puncte anorganice dicationice (S^{2-} , SO_4^{2-}), fie puncte organice obținute prin funcționalizarea ligandului organic legat de atomii de staniu cu diamine ($H_2NCH_2CH_2NH_2$, $H_2NC_6H_4C_6H_4NH_2$). În compușii heterometalici fragmentele staniu(IV)-organice se comportă ca liganzi pentru diferite metale tranziționale prin intermediul ligandului organic funcționalizat cu grupări donoare sau prin liganzi ionici legați de atomul de staniu.



$\{[2-(4'-PyCH_2N=CH_2)C_6H_4SnPh_3\}_2Cu(hfac)_2\}$

Sinteza și reactivitatea unor noi derivați fosfaalchenilici de tipul P=C-P=Y

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Compușii fosforului conținând una sau mai multe unități fosfaalchenilice de tipul $-P=C-$ sunt interesanți atât din punct de vedere al aspectelor legate de cunoștințele fundamentale dar și din punct de vedere aplicativ. Datorită multiplelor situri de reacție derivații fosfaalchenilici având unitatea $P=C-P=Y$ ($Y = O, S, Se$) sunt extrem de oferanți ca liganzi în obținerea de noi compuși coordinativi dar pot fi utilizati și ca precursori în obținerea unor cumulene.

Pentru realizarea unor sisteme cu duble legături cumulate a fost realizat un studiu de reactivitate a derivaților fosfaalchenilici conținând unitatea $P=C-P=Y$ față de derivați litiu-organici. Rezultatele studiului evidențiază un comportament diferit în funcție de grupările organice conectate la atomii de fosfor și la atomul de calcogen Y .

Evaluarea capacitatea de coordinare a derivaților difosfaalchenilici de tipul $P=C-P=Y$ prezintă de asemenea interes, atât pentru stabilizarea acestor specii cât și din punct de vedere al potențialelor aplicații. În acest sens a fost evaluat modul de conectare a $P=C-P=Y$ la metale tranziționale precum Pt, Pd, Au.

Mulțumiri

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Pincer ligands in p-block chemistry

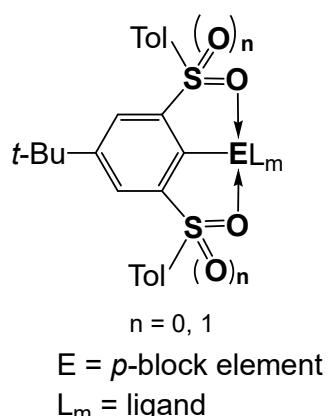
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Pincer ligands are widely used in organometallic chemistry due to their particular characteristics. They have as a main feature the ease to modify their properties by adjusting the structure (the ligand backbone and its substituents, the donor groups).¹ For this reason, lately the role of these ligands in the stabilization of heavy p-block elements also came in focus.² In the last few years our research group designed a new family of pincer type ligands,^{2,3} containing sulfonyl or sulfinyl moieties as donor groups.



Scheme 1. General structure of the pincer-type ligands used in this work

In this work we present the results obtained on the synthesis, characterization and reactivity of different *p*-block element containing derivatives supported by sulfur-based O,C,O-chelating pincer-type ligands (Scheme 1.), containing sulfonyl or sulfinyl moieties as *ortho* substituents.³

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Novel diorganotin(IV) and diorganolead(IV) complexes containing tetraphenyl dichalcogenoimidodiphosphinato ligands

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Tetraorganodichalcogenoimidodiphosphinato ligands exhibit a large variety of coordination patterns [1], but only a few studies on the synthesis and structural characterization of organotin(IV) and organolead(IV) complexes with such ligands were reported so far. Single-crystal X-ray diffraction studies on compounds of type $R_2M[(XPR'_2)(YPR''_2)N]_2$ ($R = Me, ^{2}Bu, Bz, Ph; R', R'' = Me, Ph; X, Y = O, S, Se; M = Sn, Pb$) revealed a monometallic biconnective behaviour of the bidentate ligands, thus leading to six-membered $MXYP_2N$ inorganic chelate rings. Here we report on the synthesis and structural characterization of new hypervalent (or hypercoordinated) diorganotin(IV) and new diphenyllead(IV) compounds of type $\left[\{2-(Me_2NCH_2)C_6H_4\}_2Sn\{(EPPh_2)_2N\}\right]^+[(EPPh_2)_2N]^-$, $Ph_2PbX[(EPPh_2)_2N]$ and $Ph_2Pb[(EPPh_2)_2N]_2$ ($X = Cl, Br; E = O, S, Se$). The new compounds were characterized in solution by multinuclear NMR spectroscopy ($^1H, ^{13}C, ^{31}P, ^{77}Se, ^{119}Sn$ and ^{207}Pb , as appropriate), mass spectrometry and for a few of them the molar conductivity was determined. Single crystal X-ray diffraction studies revealed hexacoordinated metal centers with monometallic biconnective organophosphorus ligands in both the diphenyllead(IV) and the diorganotin(IV) complexes, but significant structural differences are determined by the increased coordination number at tin based on $N \rightarrow Sn$ intramolecular interactions, namely a molecular structure for lead vs. an ionic structure for tin (Figure 1).

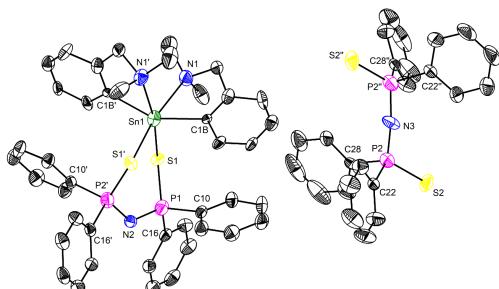


Figure 1. Thermal ellipsoids (30% probability) representation in the crystal structure of $\left[\{2-(Me_2NCH_2)C_6H_4\}_2Sn\{(SPPh_2)_2N\}\right]^+[(SPPh_2)_2N]^-$. Hydrogen atoms are omitted for clarity.

Acknowledgements

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Silver Complexes with Diorganochalcogen Ligands of Type (2-XC₆H₄CH₂)₂E (E = S, Se; X = Br, CH₃)

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Diorganoselenium compounds attracted a continuously increasing interest during last years due to their potential in organic synthesis, biology and nanomaterials [1-3]. Our recent research work was focused on the coordination behavior of diorganochalcogen ligands of type (2-BrC₆H₄CH₂)₂E [E = S (**1**), Se(**2**)], (2-CH₃C₆H₄CH₂)₂E [E = S (**3**), Se(**4**)] towards silver. The four ligands were prepared by reacting 2-bromobenzil bromide or 2-methylbenzil bromide with the corresponding sodium chalcogenide, based on adapted literature procedures [4]. All four compounds were employed in reactions with AgNO₃, AgOTf and AgClO₄ in a 1:1 molar ratio. We observed that they behave as neutral ligands towards silver. The selenium containing ligand (**2**) and the silver(I) complexes were investigated by mass spectrometry, multinuclear NMR and IR spectroscopy. The molecular structures of [(2-BrC₆H₄CH₂)₂Se], [(2-BrC₆H₄CH₂)₂SeAgOSO₂CF₃], [(2-BrC₆H₄CH₂)₂SeAgNO₃], [(2-CH₃C₆H₄CH₂)₂SeAgNO₃] and [(2-CH₃C₆H₄CH₂)₂SeAgNO₃] (Figure 1), were determined by single-crystal X-ray diffraction.

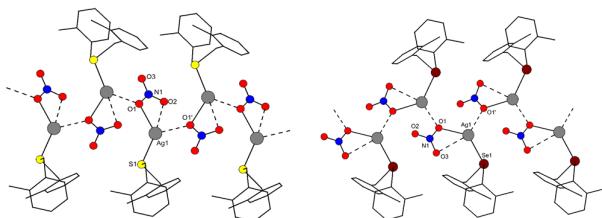


Figure 1. Supramolecular assemblies in the crystals of [AgNO₃(2-CH₃C₆H₄CH₂)₂S] and [AgNO₃(2-CH₃C₆H₄CH₂)₂Se] based on Ag···O interactions.

Acknowledgements

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Novel silver(I) complexes of organoselenium ligands bearing organic groups with pendant arms and pyrazole or phenylthiazole moieties

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The continuously growing interest in organoselenium compounds containing organic groups with pendant arms capable of N→Se intramolecular interactions was determined by their increased stability and improved properties, including biological and catalytic activity.[1] In addition, pyrazole-based derivatives are biologically active species and possess a significant ligating ability towards metal ions,[2] while thiazole derivatives were shown to be important in medicinal chemistry as antibacterial, antifungal or antitumor agents.[3] In this context, the present contribution is focused on the synthesis and structural characterization of a series of novel silver(I) complexes of previously reported heteroleptic diorganoselenides of type RR'Se (R = pyrazole (pz) or phenylthiazole (Phtz); R' = organic group with a pendant arm).[4,5] The heteroleptic ligands were prepared following literature procedures or by cleavage of the Se–Se bond in the corresponding diorganodiselenide and subsequent reaction with 1-(2-bromoethyl)-1*H*-pyrazole or 4-chloromethyl-2-phenylthiazole. The metal complexes were obtained as colorless to pale yellow solids by reacting the ligands with AgOTf in a 1:1 molar ratio in acetone in the absence of light. The new compounds were investigated by multinuclear NMR spectroscopy (^1H , ^{13}C , ^{19}F , ^{77}Se), ESI+ mass spectrometry and IR spectroscopy. Their molar conductivity in methanol solutions suggested a ionic behaviour. The molecular structures of complexes $[\text{AgOTf}\{(2-(\text{Et}_2\text{NCH}_2)\text{C}_6\text{H}_4)\text{Se}(\text{CH}_2\text{Phtz})\}]$ and $[\text{AgOTf}\{(2-(\text{O}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2)\text{C}_6\text{H}_4)\text{Se}(\text{CH}_2\text{Phtz})\}]$ were determined by single-crystal X-ray diffraction and show that the ligands act as N,Se,N chelating moieties, with both the nitrogen atom from the pendant arm and the nitrogen atom from the thiazole ring coordinated to the silver center.

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Diorganoselenides and their late d-metal complexes. Synthesis and structural characterization

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Organoselenium compounds attracted a continuous interest over the last decades due to their biological and technical importance. Of a special attention are the species bearing organic groups with nitrogen or/and oxygen atoms capable of N/O \rightarrow Se intramolecular interactions. Such interactions contribute to a significant improvement of the specific biological or catalytic activity.^[1] Diorganoselenides with OH functionalities show improved properties, either as GPx mimics or as reagents in organic synthesis.^[2] In addition, thiazole derivatives found applications as antibacterial or antitumoral agents.^[3] We report here on the synthesis and structural characterization of homoleptic diorganoselenides of type R₂Se (R = 2-(Me₂NCH₂)C₆H₄, CH₂C(OH)Me₂, CH₂phtz (phtz = phenylthiazole), as well as their silver(I) and copper(II) complexes. The diorganoselenium ligand [2-(Me₂NCH₂)C₆H₄]₂Se was prepared following the ortho litigation route,^[4] while the ligands [CH₂C(OH)Me₂]₂Se and [CH₂phtz]₂Se were obtained by reacting a mixture of Na₂Se and 1-chloro-2-methyl-2-propanol or 4-chloromethyl-2-phenylthiazole. The metal complexes were obtained by reacting the diorganoselenides with various metal salts. The new silver(I) complexes were characterized by multinuclear NMR spectroscopy (¹H, ¹³C, ¹⁹F, ⁷⁷Se, as appropriate), mass spectrometry and molar conductivity, while the new copper(II) complexes were characterized by UV-Vis spectroscopy and mass spectrometry. The molecular structures of complexes [2-(Me₂NCH₂)C₆H₄]₂SeAgOTf, [2-(Me₂NCH₂)C₆H₄]₂SeAgNO₃, [2-(Me₂NCH₂)C₆H₄]₂SeCu(NO₃)₂, [CH₂C(OH)Me₂]₂SeAgOTf were determined by single-crystal X-ray diffraction.

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