University of Bucharest

Faculty of Chemistry

ASC-UB

Students Scientific Communications Session
The 13th Edition

Book of Abstracts

May 26, 2017

Bucharest, Romania

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Faculty of Chemistry

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Content

INVITED LECTURES

Sol-gel Chemistry. Basic Researches and Applications

Maria Zaharescu

"Ilie Murgulescu" Institute of Physical Chemistry of the Romanian Academy, Splaiul Independenţei 202, 060021 Bucharest, Romania

Among the non-conventional wet chemical processes of obtaining oxide nanostructures, the sol-gel method is one of the mostly used and studied as well. As it is well known, the sol-gel process represents the formation of an inorganic polymeric network by reactions in solutions at low temperatures. In the second step the inorganic amorphous polymers could be converted by adequate thermal treatments into glasses at temperatures far lower than the melting temperature of the corresponding oxides or in crystalline materials.

The most important step of the method is represented by the formation of the amorphous inorganic polymers in solution that allows properties tailoring of the resulted products. However, this first step is the most difficult to be investigated, due to the high number of reactions that take place simultaneously leading to formation of a high number of molecular species.

In the presentation some information on the chemistry of the sol-gel processes, especially in the silica based systems, will be given based on the results of gas chromatography coupled with mass spectrometry (GC-MS). The influence of microwaves (MW) on the sol-gel process in V-doped and undoped TiO_2 systems will be also discussed based on high pressure liquid chromatography (HPLC) investigations and with thermal analysis coupled with evolved gas analysis (EGA/TG/DTA).

Preparation and complex characterization of oxide and hybrid nanostructures as films, powders (including 1D nanostructures), and nanocomposites will be also presented, as well as some of their possible applications.

Hyperpolarized Magnetic Resonance

Arnaud Comment

Cancer Research UK Cambridge Institute, University of Cambridge, Robinson Way, Cambridge CB2 0RE, UK

Nuclear magnetic resonance (NMR) is arguably one of the most prevalent and versatile spectroscopic methods in chemistry and biochemistry. It is also widely used in biomedical and medical research, in particular in conjunction with magnetic resonance imaging (MRI), for preclinical studies and as diagnostic tool in clinical environments. In the biomedical and medical fields, the high temporal and spatial resolution of MR makes it a powerful imaging modality allowing fast noninvasive detection of small morphological details even in organs rapidly moving like the heart. In fact, the modality is nowadays widespread, well accepted and contrast agents are used extensively for improved contrast or perfusion examination. MR is also a unique technique to obtain *in vivo* metabolic maps using the spectroscopic information that can be extracted from the time-domain acquisitions. In particular, it is possible to monitor the biochemical transformations of specific substrates that are delivered to subjects. Although powerful, conventional MR has a relatively poor sensitivity and it only gives access to the most concentrated substances in living organisms, most notably water. This limitation can be partially circumvented by a technique developed by physicists in the 1970s, namely dynamic nuclear polarization. Nowadays, this technique also called hyperpolarization allows recording carbon-13C images in patients to assess the severity of several diseases such as cancer.

Section 1

New Coordination Compounds based on $(Ph_2PO)_2NH$ Bidentate Ligand: Synthesis and Structural Variations

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The reaction of various metal salts, such as $Zn(ClO_4)_2 \cdot 6H_2O$, $Cu(ClO_4)_2 \cdot 6H_2O$, and $Co(ClO_4)_2 \cdot 6H_2O$, with the bidentate ligand $(Ph_2PO)_2NH$ leads to the synthesis of three new coordination compounds. All compounds have been characterized by elemental analysis, IR and UV-Vis spectroscopies. Their crystal structures were determined by single-crystal X-ray diffraction.

In all compounds, $(Ph_2PO)_2NH$ is deprotonated and coordinated as chelating bidentate ligand. The molecular structure of compound **1** was established by X-ray diffraction studies which revealed its mononuclear nature $Zn[(Ph_2PO)_2N]_2$. Zinc(II) atom is four-coordinated with tetrahedral geometry. Compound **2** is a dinuclear Copper(II) complex in which the two metal atoms are bridged by two methoxy groups. It has the molecular formula $[((Ph_2PO)_2N)Cu(\mu_2\text{-}CH_3O)]_2$. Both Cu(II) atoms are four-coordinated with square-planar geometry as seen in Figure 1. Starting from Cobalt(II) salt was obtained compound **3** which has a cubane-like $\{Co_4O_4\}$ core with metal atoms and oxygen atoms occupying alternating vertices.

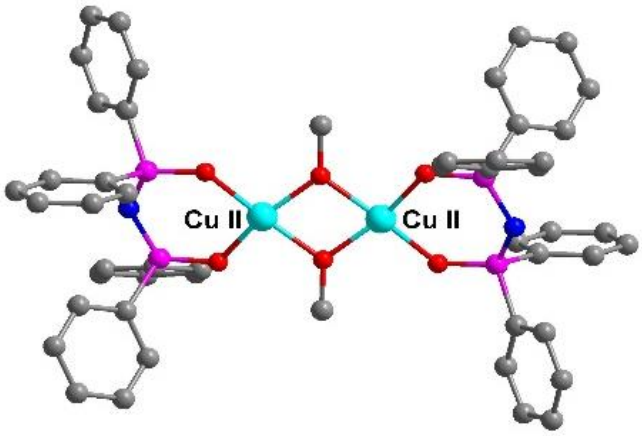

Fig. 1. Molecular structure of dinuclear compound **2** (Hydrogen atoms were omitted for clarity).

Spectrometric and voltammetric investigations of obidoxime

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Obidoxime (1, 1'-[oxybis (methylene)]bis{4-[(E)- (hydroxyimino) methyl] pyridinium) (OBD) belongs to the oximes group, which are pharmacologically active compounds, known as acetylcholinesterase (AChE) reactivators, and used for the treatment of intoxications with organophosphates and/or nerve agents[1]. OBD structure indicates that this molecule can be involved in both acid-base and redox equilibria, respectively. Thus, this work presents the behavior of OBD in these two types of equilibria. Absorbance measurements were performed in the pH-range 2 – 13. For pH values above 6.5 the overlaid spectra emphasized two isosbestic points indicating that three species are involved in these acid-base equilibria[2]. Electrochemical techniques have been proven to be useful tools in studying biologically important redox processes. The electroactive centres of OBD are the oxime groups. Cyclic voltammetry on the glassy carbon electrode in phosphate buffer solution pH=9.4 showed that OBD presents an irreversible, well-defined oxidation peak at potentials around 600-700 mV and an ill shaped broad sholder at higher potentials. The oxidation peak is due to a 2 electron diffusion controlled oxidation of one of the oxime groups whereas the more positive broad wave to the other.[3] OBD reduction generates four irreversible and diffusion controlled waves. Differential pulse voltammetry was used for quantitative applications.

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[3] I. Novak, Š.Komorsky-Lovrić, S. Žunec, A. L. Vrdoljak, Anodic Behaviour of Some Bispyridinium Oximes on a Glassy-Carbon Electrode, *Int. J. Electrochem. Sci*., 8 (2013) 9818-9834.

Self-Assembled Oligonuclear Complexes and Coordination Polymers using Triphenyltin(IV) Building Blocks

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Three new polynuclear complexes with triphenyltin(IV) as building blocks have been synthesized. All compounds were characterized in solid state using standard spectroscopic techniques (FT-IR, UV-Vis), elemental analysis, and single crystal X-ray diffraction.

The first compound is a tetranuclear complex with a {Ni-Sn-Sn-Ni} metal sequence, in which two $Ni(ampy)_2$ and two Ph_3Sn moieties are united by three biphenyl-4,4`-dicarboxylate linker. The Sn(IV) atoms are pentacoordinated, with trigonal pypiramidal geometry, while the Ni(II) atoms are hexacoordinated with distorted octahedral geometry.

Two new 1-D coordination polymers were obtained by reactions of Ph_3SnCl with 1,3,5-benzenetricarboxylic acid (trimesic acid, H_3tma) in the presence of $[Ni(ampy)_2(NO_3)_2]$ and 4-aminopyridine, respectively.

Therefore, complexes **2** and **3** are monodimensional coordination polymers formed by coordination of trimesate anion, completely deprotonated, to Ph_3Sn units. In both polymers, tin atoms have two different geometries: tetrahedral and trigonal bypiramidal. The linear chains of compound **2** forms due to the presence of $[Ni(ampy)_2(NO_3)_2]$ a supramolecular network as seen in Figure 1. Compound 3 has a zigzag structure with 4-aminopyridine connecting two chains by π-π staking and intramolecular hydrogen interactions stabilizing this compound.

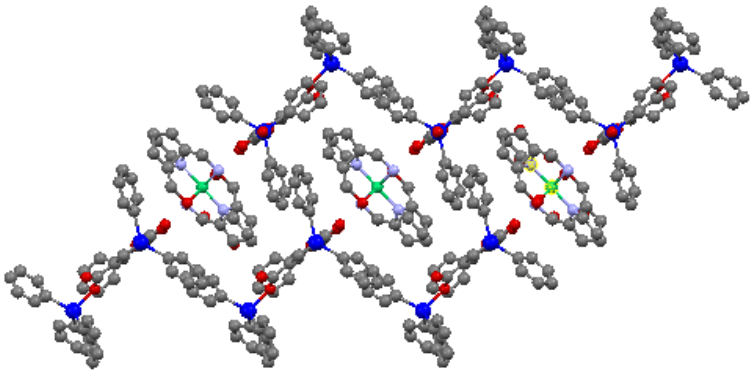

Fig. 1. Molecular structure of compound **2** (Hydrogen atoms were omitted for clarity).

Engineering Yeast Cells for Enhanced Heavy Metal Accumulation by Targeting Carboxy-rich Oligopeptides to Cell Membrane

Ghionescu Alina-Veronica[1], **Lavinia L. Ruță**[1]

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Accumulation of heavy metals without developing toxicity symptoms is a phenotype restricted to a small group of plants called hyperaccumulators, whose metal-related characteristics suggested the high potential in biotechnologies such as bioremediation and bioextraction. In an attempt to extrapolate the heavy metal hyperaccumulating phenotype to yeast, we obtained *Saccharomyces cerevisiae* cells armed with artificial metal-binding oligopeptides targeted to the inner face of the plasma membrane, expected to sequester the metal ions that penetrate the cell. In this study, we describe the construction of *Saccharomyces cerevisiae* strains overexpressing carboxy-rich oligopeptides bound to the *C*-terminus of a myristoylated green fluorescent protein (*myr*GFP). A collection of carboxy-rich oligopeptides (6-9 residues) was investigated against an array of heavy metals in terms of metabolic changes, growth defects and heavy metal (hyper)accumulation. We show that oligopeptides with alternating glutamate and aspartate residues were promising candidates in generating accumulating strains.

Ethane oxydehydrogenation over tin (SnP_2O_7) and titanium (TiP_2O_7) pyrophosphates catalysts

Ştefan-Bogdan Ivan 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, Blv. Regina Elisabeta, 030018 Bucharest, Romania

Ethane oxydehydrogenation (ODH) is an attractive alternative to conventional ethylene production via steam cracking [1]. Both tin and titanium pyrophosphates were shown to be effective catalysts for the ODH of *n*-butane [2], but they have never been studied in ethane ODH.

In this work, two titanium and two tin pyrophosphates, each of them prepared by two different methods and, therefore, having different characteristics, were studied as catalysts in ethane ODH. Thus, two well crystallized pure pyrophosphate phases with low surface areas, i.e. 6 and 4 $m^2\ g^{-1}$ for TiP_2O_7 (noted TiP-LS) and SnP_2O_7 (SnP-LS), respectively, were prepared by the reaction of the corresponding metal oxide with H_3PO_4. Also, two poorly crystallized but with high surface areas, i.e. 107 and 101 $m^2\ g^{-1}$ for TiP_2O_7 (TiP-HS) and SnP_2O_7 (SnP-HS), respectively, were prepared by the sol-gel method starting from the corresponding metal chlorides and H_3PO_4. The most active catalyst was TiP-HS within all the temperature range studied (450-700 °C), and the catalytic activity decreased following the order: TiP-HS >> TiP-LS > SnP-HS > SnP-LS. Notably, the high surface area systems were both more active and more selective than the corresponding low surface area ones. The best ethylene yield was obtained with the TiP-HS catalyst.

Acknowledgments

S. B. Ivan and I. C. Marcu thank UEFISCDI for the Young Researcher Fellowship awarded under the contract no. 5/05.01.2015 and extended until September 2017.

[1] C. A. Gärtner, A. C. van Veen, J. A. Lercher, ChemCatChem 5 (2013) 3196.
[2] I. C. Marcu, I. Săndulescu, J. M. M. Millet, Appl. Catal. A 227 (2002) 309.

Oligonuclear Copper Complexes Based on Pyrazoles.

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The pyrazoles are driving reach coordination chemistry, due to multiple coordinating modes. Aside, copper can adopt a large variety of coordination numbers and geometries and shows flexibility in supramolecular complex structures. Together are parts of superoxide-dismutase (SOD), the enzyme that catalyzes the conversion of superoxide radicals to O_2 and H_2O_2. Looking for new models for SOD, we synthesized and analysed two new polynuclear copper complexes based on 2,2'-bipyridil and 3,5-dimethyl-4-nitropyrazole (Fig.1.a.) and 3,5-dimethyl-4-iodopyrazole (Fig.1.b). The first one, (**1**) is a tetranuclear complex with pyrazole, nitro group,hidroxo and water molecules as bridging ligands since the second one, (**2**) is a binuclear systems with pyrazole and iodine as bridging ligands.

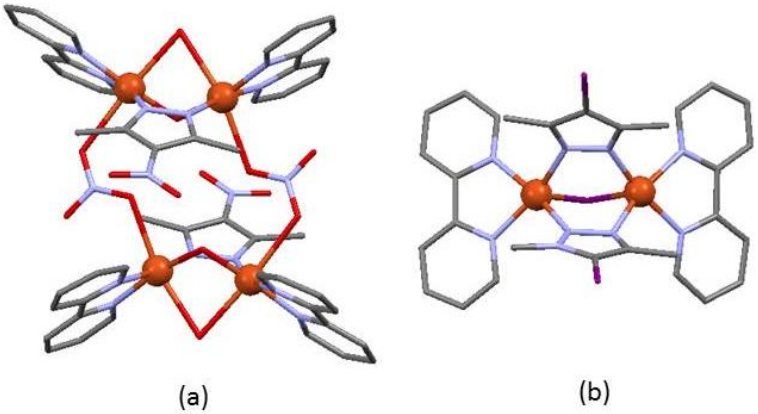

Fig. 1. The molecular structures of (**1**) and (**2**) copper complexes. The hydrogen atoms, solvents and outer ions are omitted for clarity.

Anchoring oligohistidyl-tagged GFP to the inner face of the plasma membrane of *Saccharomyces cerevisiae* cells leads to Ni^{2+} and Co^{2+} accumulation

Ana-Maria Pantazică

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Heavy metal pollution represents a threat to water supplies, soils, human and animal health, whereas the deficiency is considered equally deleterious for any form of life, or for important economic activities, such as agriculture. Heavy metals are challenging pollutants, as they are natural components of the earth's crust, they are persistent in the environment and they are non-degradable. Under such circumstances, removal of contaminating metals by means of (micro)organisms is often the method of choice, and obtaining resistant species which can accumulate heavy metals from contaminated sites represents a pre-requisite for bioremediation techniques. In this study we present the possibility to engineer yeast cells armed for heavy metal hyperaccumulation by targeting oligohistidyl-tagged GFP to the inner face of the yeast plasma membrane. Oligohistidyl residues were genetically fused to the cDNA encoding a myristoylation green fluorescent protein variant (*myr*GFP) and expressed in *Saccharomyces cerevisiae* cells. The *myr*GFP cassette introduced a yeast myristoylation sequence which allowed directional targeting to the inner face of the plasma membrane along with direct monitoring of the intracellular localization of the recombinant protein by fluorescence microscopy. We generated yeast strains which expressed *myr*GFP-His6 or *myr*GFP-His9, along with the control *myr*GFP. These strains were investigated under high metal conditions in order to identify strains which exhibit the (hyper)accumulation phenotype without developing toxicity symptoms.

New Anderson-like hexanuclear vanadium (IV) cluster

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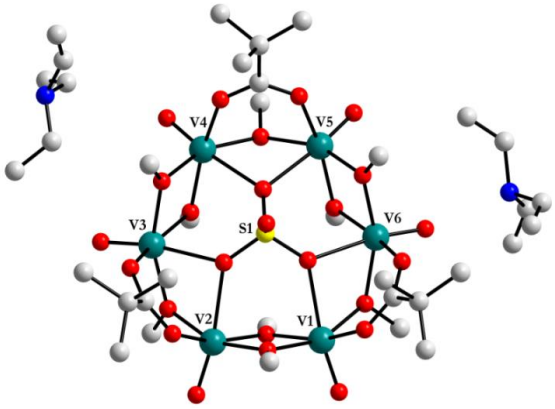
Inorg. Chem. Lab., Faculty of Chemistry, University of Bucharest, Dumbrava Roşie 23, Bucharest 020462

Vanadium-containing compounds have been investigated for a wide variety of applications, such as magnetic materials, catalysts, cathode materials, secondary building units, in the pharmaceutical industry due to the ability to mimic insulin, but also in the refining process of crude oils.[1]

Owing to the multiple oxidation states (ranging from −2 to +5) and the variable coordination geometries (including VO_4 tetrahedra, VO_5 square pyramids or VO_6 octahedra), vanadium chemistry is still widely investigated.

Y.T. Zhang and collaborators synthesized $[V_6O_6(OCH_3)_9(\mu_6\text{-}SO_4)(COO)_3]^{2-}$ polyanions serving as 3-connected secondary building units, by varying di- and tricarboxylic acids.[2]

Herein is presented the isolated monomer unit containing the $\{V^{IV}_6O_{25}S\}$ core, which adopts Anderson prototype structure. Although the metallic center presents the same coordination sphere, the monomer has never been isolated before. The X-ray crystal structure of the hexanuclear cluster $[(V^{IV}O)_6(piv)_3(OCH_3)_9(SO_4)]\cdot 2NH(CH_2CH_3)_3$ (piv - pivalate anion) is given below.



[1] A.J. Cortese, B. Wilkins, M.D. Smith, J. Yeon, G. Morrison, T.T. Tran, P.S. Halasyamani, H.C. Loye, *Inorg. Chem.*, 2015, 54, 4011–4020.
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Conceptual design of the ammonia production plant to improve energy efficiency

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The purpose of this paper is to improve the energy efficiency of an ammonia production plant, which is achieved through the thermal integration of the reaction system.

The synthesis of ammonia is based on an intensive process of energy so that the relatively large amounts of heat recovered, the greater the savings in total utilities.

What is important in a process is to take into account both the correct management of the costs of all equipment and the reduction of energy consumption for a sustainable development of the plant, implicitly of the process itself by the quality of the basic product. There was a considerable reduction in consumed resources(utilities) in the petrochemical industry using thermal integration.

Such encouraging goals together with a solid knowledge base facilitate the process improvement. The results of the research will be detailed by presenting a simulation of the ammonia production process, carried out with the help of specialized software for simulation of chemical processes.

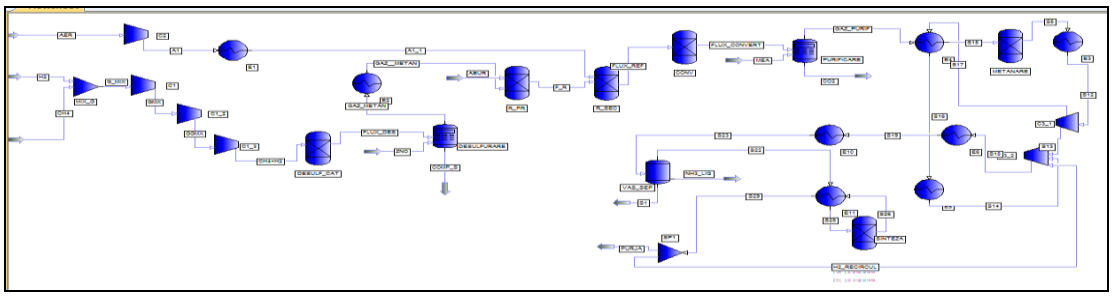

Fig. 1. Conceptual design of the ammonia production plant

Synthesis of a novel polyaminopolycarboxylic derivative

Marius C. Stoian, Anca G. Coman, Codruţa C. Paraschivescu, Mihaela Matache

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Polyaminopolycarboxylic compounds represent some of the most widely used chelators for the coordination of metal ions, *i.e.* diethylenetriamine pentaacetic acid (DTPA). The ability to provide high denticities via a hard base binding core (carboxylate ions and tertiary amines), made them suitable ligands for lanthanide ions,[1] yielding complexes with applications in imaging[2] or protein labelling.[3]
Herein we describe synthesis of some intermediates in the preparation of the methyl protected polyaminopolycarboxylic derivative which contains the iminodiacetate moiety (Figure 1).

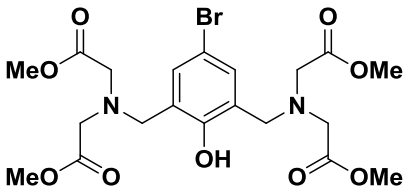

Fig. 1. The polyaminopolycarboxylic derivative

All synthesized compounds were purified and characterized by spectral analysis (nuclear magnetic resonance).

[1].A. Mohamadi, L. W. Miller, *Tetrahedron Letters* 2017, 58, 1441-1444.
[2] C.S. Bonnet, F. Buron, F. Caillé, L. Pellegatti, *Chem. Eur. J.* 2012, 18, 1419-1431.
[3] N. Candelon, N.D. Hădade, M. Matache, J.-L. Canet, F. Cisnetti, D.-P. Funeriu, L. Nauton, A. Gautier, *Chem. Commun.* 2013, *49*, 9206-9208.

The synthesis of a new heterometallic $Co^{III}Co^{II}_3Fe^{III}_3$ cluster with a frustrated Heisenberg star topology

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Current research on heteropolynuclear clusters of transition metal ions is partially motivated by a plethora of possible properties such as catalytic activity and slow magnetization relaxation in single-molecule magnets (SMMs).[1]

The versatility of these systems arises not just from the electronic properties of the transition metal ions, but also from the ability of aminoalcohol and carboxylate ligands to bond in multiple ways, allowing for new interesting topologies to occur.

Ayuk. M. Ako *et al.* have previously used the bottom-up method to synthesize a heptanuclear cluster containing only Fe(III) ions with H_3tea (triethanolamine) and Hpiv (pivalic acid) as ligands.[2]

Relying purely on self-assembly, we have synthesized a new isostructural cluster with the molecular formula $[Co^{III}Co^{II}_3Fe^{III}_3(OH)_3(Htea)_3(piv)_9(H_2O)_3]$ (1).

This compound has been characterized by single-crystal X-ray diffraction, UV-Visible spectroscopy and IR spectroscopy.

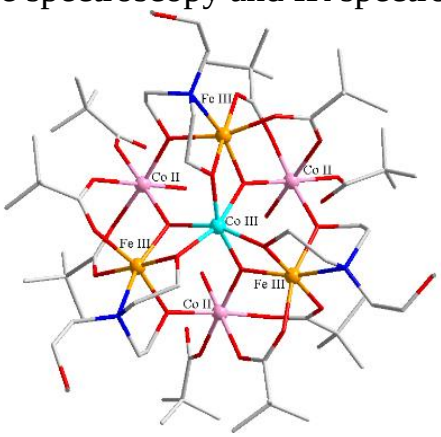

Fig 1. Structure of compound (1)

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[2] A. M. Ako, O. Waldmann, C. E. Anson, V. Mereacre, H. U. Gudel, F. Klower, A. K. Powell, I. J. Hewitt, *Inorganic Chemistry*. **2007**, 46, 3, 756-766

Influence of Triorganotin(IV) Nodes on Dimensionality of New Fumarate Polynuclear Systems

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A new series of 0-D, 1-D, 2-D, and 3-D coordination compounds with triorganotin(IV) nodes and fumarate anion as *spacer* has been synthesized. All compounds have been characterized by elemental analysis, IR spectroscopy, and single crystal X-ray diffraction.

Compound **1**, $[(Ph_3SnCl)_2(\mu_4\text{-fumarate})[(Ph_3Sn\text{-bipy})_2]$, a 0-D complex, contains a tetranuclear triphenyltin(IV) fumarato-cluster. The tin atoms have trigonal bipyramidal geometry, with the phenyl groups in equatorial positions and an oxygen atom from the fumarate ligand in one axial position. The second axial position is occupied at two opposing tin atoms by the monodentate 4,4'-bipyridyl ligand, and at the other two tin atoms by chlorine atoms maintained from the starting reagent. Complex **2**,$\{[Ph_3Sn(CH_3OH)]_2(\mu_4\text{-fumarate})[(Ph_3Sn)_2(\mu_2\text{-fumarate})]\cdot CH_3OH\}_n$, is a 1-D coordination polymer in which the tetranuclear triphenyltin(IV) fumarato-clusters from compound **1** are linked by bidentate fumarate *linker*s. Replacing the starting reagent Ph_3SnCl with Me_3SnCl and Bu_3SnCl, respectively, two new compounds have been obtained. Single crystal X-ray diffraction studies revealed a 2-D framework with a brickwall-like network topology for compound **3**. The 3-D extended structure of complex **4** is depicted in Figure 1.

Biological activity of all compounds is under investigation.

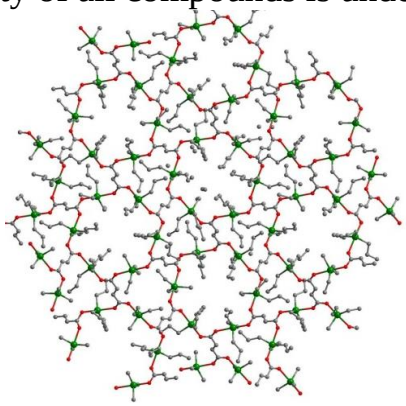

Fig.1. Molecular structure of compound **4** (Hydrogen atoms were omitted for clarity).

Section 2

Synthesis, structure and properties of novel 1,3,4-oxadiazoles-based ligands for metal-ions

Cătălin C. Anghel,[1] Mihaela Matache,[2] Codruța C. Paraschivescu,[2] Augustin M. Mădălan,[1] Marius Andruh[1]

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2,5-Disubstituted-1,3,4-xxadiazoles were firstly developed as electron transporting and luminescent molecules useful for Organic-Light Emitting Diodes (OLEDs).[1] Recently, their applications has extended to the fields of coordination polymers, metal-ion complexes or co-crystal preparation. [2]

Herein we describe the design and the synthetic approach of new 2,5-disubstituted-1,3,4-oxadiazoles (Figure 1) as ligands for coordination polymers and co-crystals. The synthesized compounds were characterized by spectral analysis (NMR spectroscopy, mass spectrometry) to confirm their identity. Investigation of the structural particularities and the electronic and optical properties by single crystal X-Ray Diffraction and solution and solid state fluorescence spectroscopy are also described.

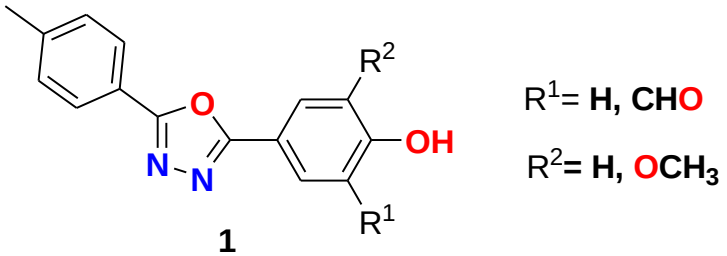

Fig. 1. *Structure of the non-symmetrical 2,5-disubstituted-1,3,4-oxadiazoles*

[1] P.K. Abhishek, C.J. Tonzola., A.Babel, A.S.Jenekhe, *Chem. Mater.*,**2004**, *16*, 4556.
[2] a) C. Anghel, M. Matache, C.C. Paraschivescu, A.M. Mădălan, M. Andruh, *Inorg. Chem. Commun.* **2017,** *76, 22: b*) L. Tang, Z. Zheng, Z. Huang, K. Zhong, Y. Biana, R. Nandhakumar, *RSC Adv*. **2015**, *5*, 10505. c) M. Du, Z.-H. Zhang, X.-J. Zhao, H. Cai, *Cryst. Growth Des.* **2006**, 6, 114.

Novel heterometallic clusters $Co^{II/III}$ - Ni^{II} clusters containing aminoalcohols and carboxylate anions

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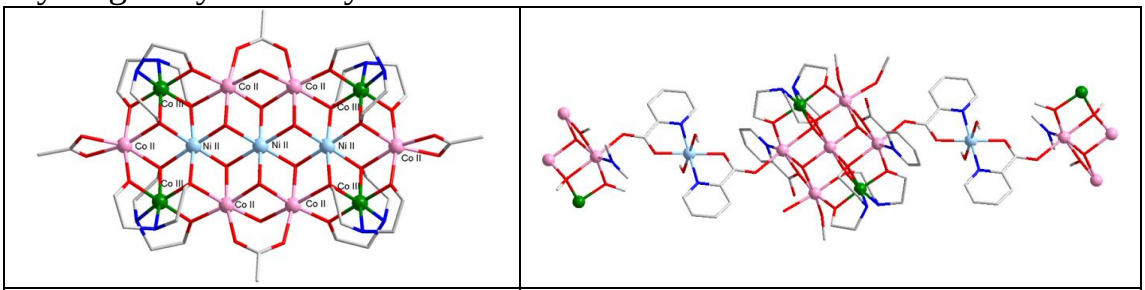
Transitional metaloclusters continue to attract a great deal of interest, partly because of their fascinating physical properties and partly for the beauty and complexity of their structures.

High-nuclearity metal complexes have attracted attention as nanoscaled functional materials in diverse application such as catalysts and electronic, photochemical and magnetic devices.[1]

Novel high nuclearity Co(II/III)-Ni(II) complexes can be isolated from relatively simple reaction. Thus, reaction between diethanolamine (H_2dea), $Ni(ClO_4)\cdot 6H_2O$ and $Co(AcO)_2\cdot 4H_2O$ in presence of triethylamine and ethanol afforded two oligonuclear clusters, one heptanuclear and one containing 13 metallic ions in the structure (1). By changing the diethanolamine with a similar aminoalcohol, N-methyldiethanolamine, the same tridecanuclear cluster was obtained. A similar system, containing H_2dea and picolinate anion (Pic^-) instead of acetate (AcO^-) leads to a polynuclear chain formed by heptanuclear clusters linked by mononuclear units (2).

All the compounds have been characterized by elemental analyses, IR and UV-VIS spectroscopy and the crystal structures were determined by single-crystal X-ray diffraction.



(1) (2)

Fig. 1. Structure of compounds 1 and 2

[1] (a) G. Mezei, C. M. Zaleski, V. L. Pecoraro, *Chem. Rev.*, **2007**, 107, 4933.
(b) M. N. Leuenberger, D. Loss, *Nature* **2001**, *410*, 789.

Synthesis of Nb-based molecular sieves: catalytic properties-catalytic performances correlation

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In the context of the actual needs connected with the catalytic biomass transformation to valuable products [1], herein we present the two-step synthesis of a series of Nb-silicalite and Nb-Beta zeolites and their application in the HMF synthesis through glucose dehydration. The synthesized Nb-based materials were exhaustively characterized using XRD, TG-DTA, Raman and IR spectroscopy. Activity tests were carried out using glucose as raw material in an aqueous phase, at 150-210°C and 12-24 h. For comparison, pristine H-BEA zeolites with different Si/Al ratios (18 - β1; 6 - β2; 12 - β3) were also tested.

Characterization results revealed the successful incorporation of Nb in the zeolite framework. Shortly, while XRD revealed the Nb-incorporation did not affect the crystallinity of the parent molecular sieves, the new IR small intensity band at 3743 cm^{-1} can be related to the presence of the Nb(V)O-H groups while the new band at 952 cm^{-1} it is taken as an indication of the presence of Si-O-Nb units in the framework of the Nb-β materials, in perfect accordance with [2]. Highly important, the new materials display higher stability in hot water than the pristine Beta zeolites.

The Nb-based catalysts are efficient for the selective dehydration of glucose to HMF (> 53%). The optimum catalyst and optimal reaction conditions as well as the catalytic performances - catalytic properties correlation, revealing the most promising Nb-BEA zeolite catalyst with the ideal features for the efficient HMF synthesis will be discussed in detail.

[1] F. Yang, Q. Liu, X. Bai, Y. Du, *Bioresource Technol*. 102, 3424 (2011)
[2] F. Tielens, T. Shishido, S. Dzwigaj, *J. Phys. Chem. C* 114, 3140 (2010)

Electrochemistry and antibacterial evaluation of azulene-containing chalcones

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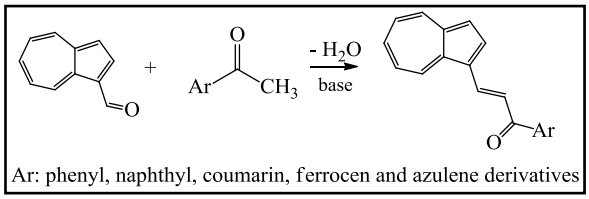
Chalcone derivatives exhibit many pharmacological properties, such as cytotoxic, antioxidant, antimicrobial, antiviral, anti-inflammatory, antimalarial, and last but not least anesthetic activities. They have close relationship with flavones, aurones, and tetralones and serve as valuable synthons for preparation of biological relevant heterocyclic compounds. Moreover, chalcones were found to show excellent non-linear optical response, fluorescence and electrochemical properties.

There were synthesized several novel chalcones with azulene moiety in their structure *via* Claisen-Schmidt condensation of aromatic ketones with azulen-carbaldehyde, in the presence of organic or inorganic bases (Scheme 1). The azulene-tailored chalcones are intensely colored compounds, soluble in dichloromethane, ethyl acetate and acetonitrile, but less soluble in polar protic solvents such as ethanol.



Scheme 1

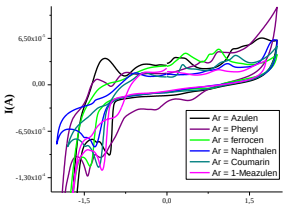


Fig.1.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) revealed similar electrochemical profile of all studied compounds with a well-defined irreversible cathodic peak corresponding to the reduction of the carbonyl group between (-1.4) - (-1.3) V (Figure 1). The electrochemical properties were carried out in acetonitrile solution containing 0.1 M Bu_4NClO_4 as supporting electrolyte. The antibacterial activity of these azulene-containing chalcones was evaluated on a panel of five fungi, gram positive and gram negative bacteria by determining the minimum inhibitory concentration (MIC). Analysis of the results showed that azulene substitution led to compounds with appreciable activity against *Candida albicans* and *Enterococcus faecalis* with best MIC value of 19 μg/mL.

Synthesis and Structural Characterization of New 1-D and 2-D Copper Coordination Polymers

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Two new coordination compounds $\{[Cu(BF_4)(\mu_2\text{-bpp})_2](BF_4)\cdot azopy\}_n$ (compound **1**), and $\{[Cu(\mu_2\text{-}BF_4)(\mu_2\text{-bpp})_2(H_2O)](BF_4)\cdot azopy\}_n$ (compound **2**), have been obtained by reactions of $Cu(BF_4)_2\cdot 6H_2O$ with the flexible ligand 4,4'-trimethylenedipyridine (1,3-bis(4-pyridyl)propane, bpp), as bidentate spacer, in the presence of 4,4'-azopyridine (azopy). The two compounds were obtained as single crystals and characterized in solid state using standard spectroscopic techniques (FT-IR, UV-Vis-NIR), elemental analyses, and single crystal X-ray diffraction.

The single-crystal X-ray analyses showed that compound **1** is a one-dimensional polymer, while compound **2** has a two-dimensional structure. Molecular structure of compound **1** is depicted in Figure 1. It has a chain-like structure with Copper(II) atoms double-bridged by the bidentate diamine ligand bpp. The azopy molecules have two different orientations around the polymer chains.

Complex **2** is built up by bridging the chains of compound **1** through BF_4 anions acting as bidentate ligand. The planes were held together by hydrogen interactions between the water molecules coordinated into the axial positions of Cu(II) and azopy molecules *via* water molecules from the crystal, thus yielding a 3-D extended supramolecular network.

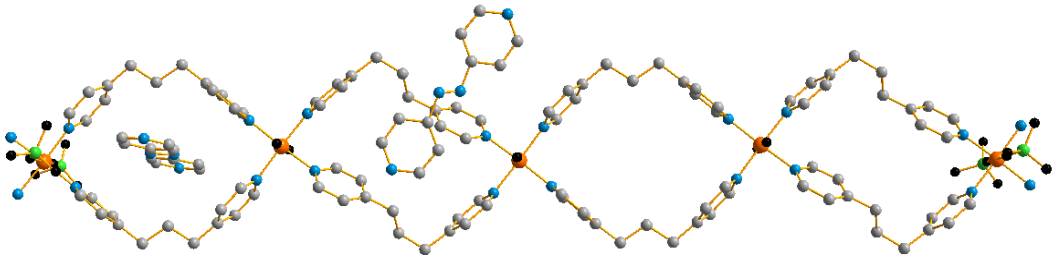

Fig. 1. The chain-like structure of compound **1**, $\{[Cu(BF_4)(\mu_2\text{-bpp})_2](BF_4)\cdot azopy\}_n$ (H atoms were omitted for clarity).

Electrochemical characterization of some extracts obtained from seeds, pulp and skin of red grapes

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Phytochemical compounds obtained from differents vegetal materials are the subject of many studies in the last years. The interest of scientists for red grapes in treatment of different ailments is related to the presence of polyphenols.

The samples analyzed are represented by six alcoholic extracts obtained from seeds, skin, pulp and juice of two varieties of red grapes: black Feteasca (FN) and large Burgundy (BM).

The objectives of this study were to determine the total polyphenol content of alcoholic extracts and corelate it with antioxidant activity.
The methods by which the antioxidant activity of the extracts was revealed were cyclic voltammetry and differential pulse voltammetry to higlight the capacity of samples to reduce various free radicals from human body and polyphenols dosing has been achieved using Folin-Ciocalteu method.

The results of this study show that each extract obtained from two varieties of red grapes has antioxidant capacity, but in different proportion. Differential pulse voltammograms realized for all samples obtained from various parts of FN and BM red grapes show that only in the case of extracts from pulp and juice, intensity of oxidation peaks are bigger for FN variety than BM. Otherwise, results indicate the fact that BM grapes have a large cantity of polyphenols in skin and seeds than FN. The results obtained using electrochemical methods are according with the values for total polyphenols quantity determined by Folin-Ciocalteu method.

In conclusion, this study reveals that all alcoholic extracts have antioxidant properties because of their polyphenolic content, seed extracts from FN having the best antioxidant activity.

Synthesis of intermediates for preparation of new *N*-acylhydrazones

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N-acylhydrazones are versatile molecules that found applications in many fields for preparation of useful materials[1] or as precursors for heterocyclic compounds.[2] The great advantage of such class of compounds is represented by their convenient synthesis starting from carbonyl compounds and hydrazides of carboxylic acids.

Herein, we present synthesis of some intermediates, aldehydes and hydrazides, in the synthesis of new *N*-acylhydrazones as well as the procedural approach and physical characterisation, by spectral analysis (nuclear magnetic resonance).

[1] (a) M.N. Chaur, D. Collado, J.-M. Lehn, *Chem. Eur. J.* **2011**, *17*, 248; (b) L.A. Tatum, X. Su, I. Aprahamian, *Acc. Chem. Res.* **2014**, *47*, 2141.
[2] C. Dobrota, C.C. Paraschivescu, I. Dumitru, M. Matache, I. Baciu, L.L. Ruta, *Tetrahedron Lett.* **2009**, *50*, 1879

Coordination polymers based on fluorescein

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Despite the wide range of application of the fluorescein derivatives, examples of coordination polymers based on fluorescein as ligand are still scarce. Metal-organic frameworks (MOFs) based on fluorescein and different 3d or lanthanide metal ions can attract much attention due to the coordination versatility of fluorescein derivatives and potential applications in luminescence, sensing and hosting other molecules, catalysis and magnetism [1].

Fluorescein contains a high conjugated system which relies also on a keto-enol tautomerism and its polydentate nature can be exploited for design and synthesis of coordination polymers with or without the help of other ligand molecules [2]. Thus, 1D, 2D or 3D coordination polymers can be built using transitional or lanthanide metal ions. A Zn^{2+} 1D coordination polymer (Fig. 1) involving solely fluorescein as ligand proved to have high thermal stability, up to 400°C, and exploitable porosity.

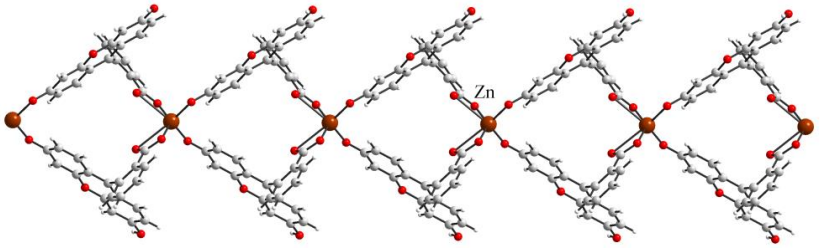

Fig. 1: Crystal structure of Zn^{2+} coordination polymer.

Based on MOFs porosity, this type of coordination polymers can be used in hosting different molecules compatible with the cavities dimensions, therefore influencing the properties of the final material.

[1] Y. Huang, T. Sheng, R. Fu, S. Hu, C. Shen, Q. Zhu, X. Ma, X. Wu, J. Huaxue, *Chin. J. Struct. Chem.* **2011**, *30*, 230-234.
[2] J. Thomas, K.S. Ambili, *J. Mol. Struct.* **2015**, *1098*, 167-174.

Michael addition catalyzed by N/doped and nano-Au platelets/Graphenes

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The Michael addition is one of the most useful methods for the formation of C-C or C-X (X=N, O, S, P) bonds in organic synthesis [1, 2]. The reaction consists in the addition of a nucleophilic compound (Michael donor) to an electron poor olefin (Michael acceptor), the resulting product being called a "Michael adduct". The Michael addition products have been proven to be valuable assets in the development of various fields, such as biomedicine, optoelectronics, composites and adhesives. [2] It has been observed that the Michael reaction needs a strongly basic catalyst and, until now, mostly liquid bases have been used. Due to its wide range of possible applications and the otherwise mild conditions that it requires, it became desirable to transform the classic Michael reaction into a heterogeneous process, with the help of proper solid catalysts, which will simplifies the product isolation procedure. The aim of this study was to to achieve high yields using N-doped graphene or Au-platelets supported on graphene [3] as solid catalysts in Michael addition reactions, using methyl vinyl ketone (MVK) as Michael acceptor and various esters (e.g. ethyl acetoacetate, ethyl 2-oxocyclohexanecarboxylate, etc.) as Michael donors. Adsorption energies for the catalysts surfaces have been calculated using DFT methods. The catalytic approach provides a facile, economical, environmentally friendly method for the synthesis of different Michael adducts (yields ~100%) under mild conditions (e.g. room temperature, water as solvent and the use of low catalyst loading due to the high activities of the catalysts) which makes the method to have many applications in organic and medical chemistry.

Dry reforming of methane over perovskite catalysis

Alina-IoanaTruşcă, Adriana Urdă, Mihaela Florea

University of Bucharest, Faculty of Chemistry,

The global concern over the rise in carbon dioxide has been increasing in the last years due to the large amounts of emissions that accumulate into the atmosphere from different sources. One of the best methods to reduce the concentration of CO_2 and CH_4 in the atmosphere is through their utilization, e.g. by dry reforming of methane (with carbon dioxide) [DRM]. Although CO_2 reforming is highly economical there are two very important downsides: high amounts of carbon are deposited on the surface of the catalyst which lead to its deactivation, and the active metal may sinter due to the high reaction temperature.

For this study we have prepared and characterized $La_{1-x}Ce_xNiO_3$ perovskite catalysts with lanthanum partially replaced by cerium (x = 0; 0.1; 0.3). Nickel was chosen because of its high activity in this reaction and low cost, while the partial replacement with cerium was intended and tested in order to inhibit the coke formation. $La_{1-x}Ce_xNiO_3$ perovskites were prepared from lanthanum, cerium and nickel nitrates, by the "citrate method". The samples were characterized by DTA-TG, XRD, and nitrogen adsorption-desorption isotherms, and then tested in the dry reforming of methane. DTA-TG analysis showed a slight endothermic peak centered at ~ 75°C due to the elimination of water, and an exothermic peak (270-420 °C) associated with the decomposition of organic residues. In XRD, all the diffraction lines for the $LaNiO_3$ catalyst can be attributed to the $LaNiO_3$ perovskite structure. When cerium is introduced new lines appear that were attributed to a separate CeO_2 phase. The BET analysis confirms the catalysts calcined at 900°C are non-porous. When cerium is introduced the specific surface area decreases, while the pore diameter increases. Tests for the catalytic activity of catalysts were performed to see the life time of the catalyst and its selectivity. We observed that the pre-reduction treatment was not necessary and the metallic Ni active phase can be obtained during the reaction. The catalytic activity reached 94.2% on $LaNiO_3$, 95.5% on $La_{0.9}Ce_{0.1}NiO_3$ and 92.9% on $La_{0.7}Ce_{0.3}NiO_3$, for CO_2, respectively 84.9%, 91.3% and 97.0% for CH_4, at 750°C. The samples were stable for approximately 175 minutes before the carbon deposition occurred.

Section 3

Synthesis and photophysical properties of profluorescent nitroxides as dual luminescent-paramagnetic probes

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2,5-Disubstituted-1,3,4-oxadiazoles display high electron mobility and good luminescent and thermal behavior. These features make them suitable materials mainly for construction of Organic-Light Emitting Diodes.[1]

Profluorescent nitroxides represent a class of compounds that combine the properties of fluorescent molecules with stable free radicals and are useful in detection of various biological analytes of interests through redox changes or radical trapping.[2] The fluorescence of the fluorescent moiety is quenched by the unpaired electron of the radical and can be restored by the nitroxide reduction to the hydroxylamine, allowing thus two techniques (fluorescence spectroscopy and electron paramagnetic resonance) to inspect their switching behavior.[2]

In this context, taking into consideration the promising luminescent properties of the oxadiazole-based compounds, we report the synthesis and photophysical investigation of new 2,5-disubstituted-1,3,4-oxadiazole-TEMPO hybrids **1a-d** (Figure 1) as profluorescent nitroxide probes.

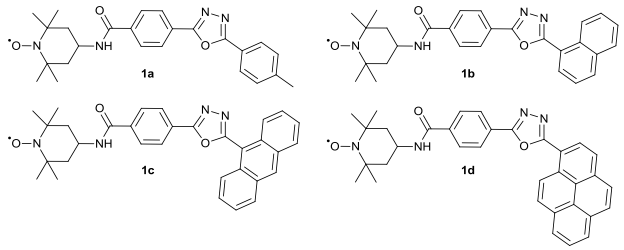

Fig.1. Structure of the new 2,5-disubstituted-1,3,4-oxadiazole-TEMPO hybrids

[1] A Paun, N.D Hadade, C.C. Paraschivescu, M. Matache, *J. Mater. Chem. C* **2016**, *4*, 8596.

[2] (a) J. P. Blinco, K E. Fairfull-Smith, B. J. Morrow, S. E. Bottle, *Aust. J. Chem* **2011**, *64*, 373; (b) A. Kaur, J. L. Kolanowski, E. J. New, *Angew. Chem. Int. Ed* **2016**, *55*, 1602.

Magnetic beads competitive ELISA for domoic acid immunoassay

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[2]University of Rome "Tor Vergata", Department of Science and Chemical Tehcnology, Via della Ricerca Scientifica, Rome, 00133, Italy

Domoic acid is an algal derived sea food toxin that functions as a glutamate antagonist. At high doses, it is responsible for the human neurotoxic illness known as amnesic shellfish poisoning. The increase in frequency, intensity and geographical distribution of domoic acid poisonings has become a growing problem worldwide [1,2].

Magnetic particles as carriers/label for the antibodies are of great interest for immunoassay configuration due to the fact that they improve the orientation of the immobilized antibody and increase the protein loading [3,4].

Herein, we report a new strategy for sensitive domoic acid determination based on magnetic beads modified competitive immunoassay. The detection of domoic acid was achieved by using a competition for the rabbit IgG monoclonal antibody anti-domoic acid between free and HRP (horseradish peroxidase)-domoic acid conjugate. An increasing of the sensitivity was achieved by using immobilising rabbit IgG policlonal antibody onto magnetic beads. 3,3',5,5'-Tetramethylbenzidine (TMB) was used as a marker of HRP enzymatic reaction. Using the competitive format of ELISA and a monoclonal antibody against domoic acid, the method proved to be fit-for-purpose to achieve low limits of detection (36 ng/l) and good sensitivity for the quantification of toxin in water samples. Assay parameters such as working ranges, liniarity domain were optimized.

[1] L. Micheli, A. Radoi, R. Guarrina, R. Massaud, C. Bala,, D. Moscone,G. Palleschi, Biosens. & Bioelectron., 20 (2), 2004**,** 190-196.
[2] L. Rotariu, F. Lagarde, N. Jaffrezic-Renault, C. Bala, Trends in Anal. Chem., TRAC, 79, 2016, 80-87.
[3] L.G. Zamfir, I. Geana, S. Bourigua, L. Rotariu, C. Bala, A. Errachid, N. Jaffrezic-Renault, Sens. And Actuators B: Chemical, 2011, 159, 178–184.
[4] L. Revertéa, B. Prieto-Simónb, M. Campàs, Anal. Chim. Acta, 2016, 908, 8–21.

A new synthetic approach towards polynuclear complexes using mixed Schiff- and Mannich base ligands

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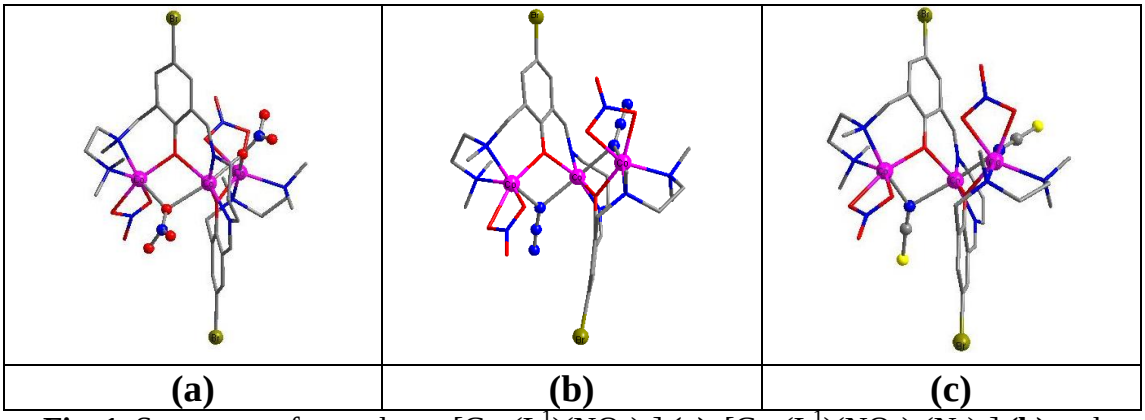
Seven new homonuclear complexes, $[Co_3(L^1)(NO_3)_4]$, **1** (Figure 1a), $[Ni_3(L^1)(NO_3)_4]$, **2**, $[Co_3(L^1)(NO_3)_2(N_3)_2]$, **3** (Figure 1b), $[Ni_3(L^1)(NO_3)_2(N_3)_2]$, **4**, $[Co_3(L^1)(NO_3)_2(NCS)_2]$, **5** (Figure 1c), $[Ni_3(L^1)(NO_3)_2(NCS)_2]$, **6**, $[Ni_6(L^2)(NO_3)_6]$, **7**, have been obtained using a *step-by-step* method where H_2L^1 and H_2L^2 have been synthesized by the condensation reaction of a Mannich base with 1,3-diaminopropane and 1,8-diamino-3,6-dioxaoctane, respectively.

The reactions of the Mannich base with 1,3-diaminopropane and $Co(NO_3)_2 \cdot 6H_2O$ or $Ni(NO_3)_2 \cdot 6H_2O$ in a molar ratio 2:1:2,5 gave complexes **1** and **2**. Compounds **3** and **4** where obtained by replacing two nitrate ions with two N_3^- ions, while complexes **5** and **6** where synthesized by replacing the two nitrate ions with two NCS^- ions. These compounds are two by two isostructural. The substitution of 1,3-diaminopropane with 1,8-diamino-3,6-dioxaoctane leads to complex **7**.

All compounds have been characterized in solid state using routine techniques (FTIR, UV-Vis-NIR spectroscopy, elemental analysis) as well as by single crystal X-ray diffraction. Also, complexes **1**, **3** and **4** have been characterized by powder X-ray diffraction.



(a) **(b)** **(c)**

Fig. 1. Structures of complexes $[Co_3(L^1)(NO_3)_4]$ **(a)**, $[Co_3(L^1)(NO_3)_2(N_3)_2]$ **(b)** and $[Co_3(L^1)(NO_3)_2(NCS)_2]$ **(c)**. Hydrogen atoms were omitted for clarity.

Coordination polymers of various topologies constructed from tetradentate spacers

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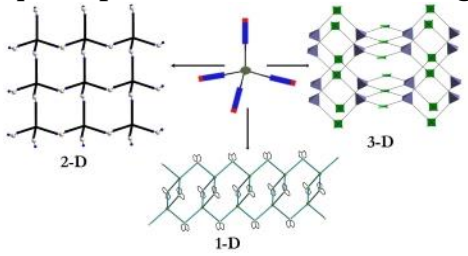
[b] *"Petru Poni" Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda, 41A, 700487 Iasi, Romania*
[c]*Centre of Supramolecular Organic and Organometallic Chemistry, Department of Chemistry, Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University, 11 Arany Janos, 400028, Cluj-Napoca, Romania*

Coordination polymers, MOF materials, are of tremendous interest, especially due to the remarkable properties they may develop, like porosity, high surface area.[1] Crystal engineering based on self-assembling directed by metal-ligand binding is focusing on tuning the properties towards functional applications. Rigid tetrahedral ligands have recently emerged as a structural-generating feature in designing coordination systems with robust, highly connected topological nets.[2] Tetradentate tectons built around a tetrahedral centre (adamantane, C, Si, Ge) are expected to generate 3-D solid state architectures based on the spatial orientation of the ligating groups.

Herein, we report the synthesis and structural characterization of several coordination polymers constructed from tetratopic spacers (adamantane, Sn or spirobifluorene derivatives) and metal-based assembling species (square planar, tetrahedral or angular nodes).



[1] (a) M. L. Foo, R. Matsuda, S. Kitagawa, *Chem. Mater.*, **2014**, *26*, 310, (b) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem. Int. Ed.*, **2004**, *43*, 2334; (c) C. Janiak, *Dalton Trans.*, **2003**, 2781;
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Chimeric design of heterospin 2p-3d, 2p-4f, and 2p-3d-4f complexes using a novel family of paramagnetic dissymmetric compartmental ligands

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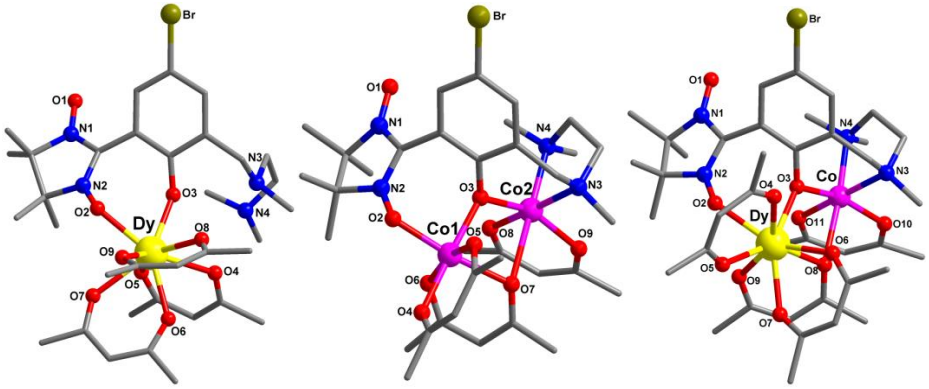
The nitronyl-nitroxide radicals played a very important role in the history of molecular magnetism.[1] End-off bicompartmental ligands bearing a nitronyl-nitroxide arm have been designed for synthesizing various heterospin molecular systems.[2] These ligands can selectively interact with 3d and 4f metal ions, leading to *2p-4f* **(1)**, *2p-3d* **(2)**, and *2p-3d-4f* **(3)** complexes (Figure 1).

The structures were obtained by single crystal X-ray diffraction. The magnetic properties of the *2p-4f* and *2p-3d-4f* complexes have been investigated. Compound **1** exhibits slow relaxation of magnetization, which indicates a Single Molecule Magnet behavior.

Chiral ligands and, consequently, chiral heterospin complexes can be obtained as well, when chiral amines are chosen.



(1) **(2)** **(3)**

Fig. 1. Perspective views of compounds **1**, **2**, and **3**.

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