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

Students' Scientific Communications Session

- The 15th Edition -

Book of Abstracts

May 24-25, 2019

Bucharest, Romania

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Alvogen

MGC

MICROSIN

Content

Pe urmele reacţiei de hidrogenare:o călătorie în timp şi printre subiecte

Prof. Dr. Vasile I. Pârvulescu

Department of Organic Chemistry, Biochemistry and Catalysis, Faculty of Chemistry, University of Bucharest

În termen simplist, reacţia de hidrogenare în chimia organică este în general introdusă ca adiţia hidrogenului la legături duble sau triple. În termen de realizare însă, această reacţie reclamă catalizatori şi condiţii experimentale specifice pentru atingerea nivelului de selectivitate dorit. Acest obiectiv nu este întotdeauna uşor de atins datorită pe de o parte dimensiunii moleculei de hidrogen şi energiilor mici implicate în scindarea acesteia, ceea ce ar părea a fi un avantaj, iar pe de altă parte complexităţii moleculelor care sunt supuse acestei reacţii, ceea ce este considerat a fi un dezavantaj.

Prezentarea discută în mod critic felul în care se poate controla aceasta selectivitate în molecule care din punct de vedere termodinamic conţin legături favorizate precum precum legăturile nesaturate C=C şi C≡C şi legături mai puţin favorizate hidrogenării precum cele din cicluri aromatice sau legăturile C=O sau N=O. Un caz şi mai complicat este acela al reacţiilor stereoslective în care chemoselectivatea trebuie completată de un control steric.

Extra-analytical applications of liquid chromatography

Prof. Dr. Victor David

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Liquid chromatography is known to have large applications in analytical chemistry as a result of its performances in qualitative and quantitative analysis of multi-component samples. Usually, it is focused on the method development and large scale applications for the environmental, pharmaceutical and biomedical analyses. Another research direction in liquid chromatography is given by the possibility to use the chromatographic process to measure many physical parameters of studied compounds that are otherwise difficult to obtain by means of extra-analytical approaches. This possibility is depending on various factors influencing the liquid chromatographic process: the composition of the mobile phase, the nature of the stationary phase and, in some cases, the type of the detection technique used in the process. Among the most important physico-chemical parameters investigated by liquid chromatography are equilibrium constants (basicity, acidity), hydrophobicity descriptors, such as the well-known octanol/water partition constant (K_{ow}), solubility data, and thermodynamic parameters (standard variation of enthalpy or entropy for the transfer of solute from the mobile phase to the surface of stationary phase). Also, liquid chromatography offers the best opportunity to study intermolecular interactions and structural stability under various solvating conditions. All these aspects of utilization of liquid chromatography in obtaining extra-analytical information about various species involved into the complex chromatographic process are presented and detailed for some specific classes of compounds, according to the recent personal achievements or reported by the literature. Also, some theories (adsorption and partition models, solvophobic theory) explaining the retention mechanism are presented and used to characterize to solute the behaviour or the chromatographic column. Thus, one of the most important parameters characterizing the chromatographic column is phase ratio, which is discussed for the reversed-phase retention mechanism.

Section 1

Synthesis of heteroaromatic thioorganic derivatives as alternative electrophilic partners in Sonogashira coupling reaction

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The Sonogashira coupling reaction is the way in which many heterocyclic compounds with interesting properties can be synthesized. The current challenges of this field are to find new electrophile partners to replace halides. Heteroaromaticthioorganic derivativesmay play the role ofalternative electrophilic partners.

Currently, thioorganic compounds such as thiols and disulfides, which are present in many biologically active compoundsreceive considerable attention due to the fact that they are widely used as building blocks in organic synthesis.[1]

Furthermore, disulfides play important roles in biological and chemical processes. The biochemical importance of the disulfide bond is also determined by the uniqueness of the nature of the thiol disulfide system in which the S-S bond can be formed under appropriate conditions for the biological process. [2]

In this paper we propose the synthesis of heteroatomaticthioorganic derivatives such as thiols and disulfides that can act as electrophilic partners.

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Synthesis of new highly emissive 2,5-disubstituted-1,3,4-oxadiazoles obtained through cross-coupling reactions

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During the past few years, there has been a tremendous interest in the synthesis of efficient materials for the fabrication of Organic Light Emitting Diodes (OLEDs). In this context, 2,5-disubstituted-1,3,4-oxadiazoles have been intesively developed and studied.[1][2] Such heterocyclic structures have a very good electron-transporting ability and also display interesting luminescence.[3] We designed and synthesized novel 2,5-disubstituted-1,3,4-oxadiazoles containing an aryl unit and an electron-donor moiety. The compounds (Figure 1) were obtained through an oxidative cyclization for closure of the oxadiazole core, followed by C-C cross-coupling reactions. Their structure was characterized by NMR spectroscopy.

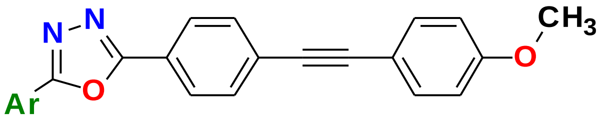

Figure 1. The structure of the target compounds

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Two new homometallic hexanuclear Co^{II}/Co^{III} clusters with N,N,N,N`-Tetrakis(2-hydroxypropyl)ethylenediamine

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The chemistry of clusters containing paramagnetic 3d-, 4f- and 3d/4f-metal ions is today an area of high interest in Molecular Magnetism and Bioinorganic Chemistry [1]. Most of these compounds are aggregated by serendipitous self-assembly, using multidentate ligands.

Following our research in the chemistry of cobalt-containing clusters [2, 3], we report now on two new hexanuclear, mixed valence Co^{II}/Co^{III} clusters, which is assembled using *N*,*N*,*N′*,*N′*-Tetrakis-(2 hydroxypropyl) ethylenediamine (H_4THPEN) as a ligand: $[Co^{II}_3Co^{III}_3(HTHPEN)_3(OH)_4]\cdot 2ClO_4^-\cdot 2H_2O$ **1**, $[Co^{II}_3Co^{III}_3(HTHPEN)_3(OH)_3(CH_3O)]\cdot 2ClO_4^-$ **2**. The crystal structure was solved by single crystal X-ray diffraction. The FTIR and UV-Vis spectra are discussed.

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Derivatization of lignin with aniline based on enzyme biocatalysis

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Introduction

In this study we propose a new way of capitalizing lignin and modulating physical properties based on the derivatization process. A new strategy has been created to introduce aniline into the lignin structure by enzymatic biocatalysis. Lignin molecule with basic phenolic structure was oxidized in the presence of aniline. Radicalic mechanism has been performed with peroxidase enzyme as catalyst and H_2O_2 as oxidation reagent. The reaction product was a derivatised polymeric structure with new C-N bonds.

Experimental

The experiments involved the derivatization of commercial lignin (alkali, acid-treated and Klason lignin) with aniline in 10 mM PBS solution (pH=8.2), peroxidase or laccase enzyme, and H_2O_2. Sometimes co-solvent was also added in order to improve the lignin solubility in aqueous phase.

Lignin and its derivatives were characterized using different techniques such as UV-VIS spectroscopy, Folin-Ciocalteu, Fourier-transform infrared spectroscopy (FT-IR), contact angle measurements, conductivity, and nuclear magnetic resonance (NMR).

Results and discussion

Lignin derivatized with aniline was investigated to determine the chemical structure and physical properties of the resulted products. The derivatization using enzyme catalysis has been set up for insertion of $-NH_2$ groups in the lignin structure. The experimental data confirmed the success of lignin derivatisation under optimum conditions set up for the biocatalytic process.

Synthesis of polyaryl compounds usingaqueous Suzuki cross-coupling reaction

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Salicylaldehydes are important building blocks in organic chemistry[1,2]. Access to their diversification can beconvenientlyachieved through metallocatalyzed coupling reactions. Among these, Suzuki coupling reaction is preferred, both in terms of tolerance to the various functional groups and possibility of using water as solvent[3]. In this paper, we present a new methodological approach for synthesis of various polyaryl dialdehydes derivatives by Suzuki cross-coupling, using water as solvent, in the presence of an in house palladium catalyst (Figure 1).

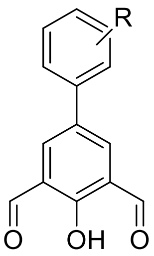

Figure 1:General structure of the synthesized polyaryl dialdehydes

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Mononuclear lanthanide complexes with tripodal ligands for amines recognition

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The tripodal ligands, as an extension of the podand concept to three dimensions, represent a category of molecules able to encapsulate more fully their guest. The Schiff-base tripodal ligand tris[4-(2-hydroxy-3-methoxyphenyl)-3-aza-3-buten]amine, obtained from *o*-vanillin and tris(2-aminoethyl)-amine, proved its capability to coordinate one or two lanthanide ions, the binuclear compounds representing models for the study of magnetic interactions between lanthanide ions.

The mononuclear lanthanide complexes with this ligand can be used for recognition of the ammonium cation (figure 1) or different protonated amines by hydrogen interactions. The interest for such complexes is justified by the potential biomedical application: contrast agents in magnetic resonance imaging or luminescent sensors responsive to biological amines.

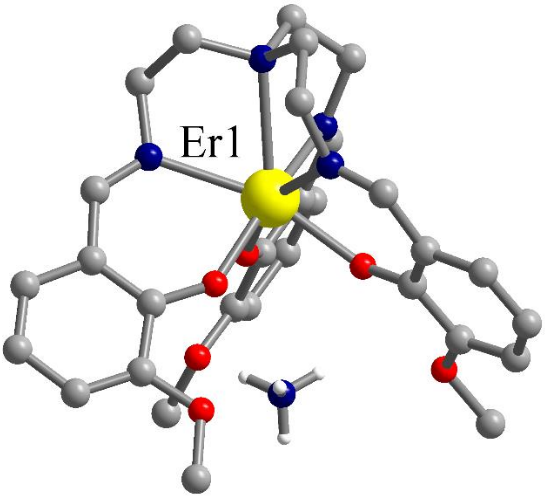

Figure 1. Perspective view of the complex [Er(valtren)(NH_4)]$^+$ in solid state (the structure was determined by X-ray diffraction on single crystal)

Anion dependent self-assembly of copper(II) coordination polymers

**<u>Diana Ioana Stăncuţ</u>, Cristina Mozăceanu, Andrei Alunel Pătraşcu,
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Self-assembled coordination polymers have received great attention in recent years due to their structural diversities and also to their wide array of potential applications in many fields including gas storage, catalysis, magnetism, luminescence, and ion exchange [1].

This paper focuses on the synthesis of new coordination polymers of copper(II) by node-and-spacer strategy, using various copper(II) salts: $Cu(BF_4)_2·6H_2O$, $Cu(ClO_4)_2·6H_2O$, $Cu(CF_3SO_3)_2$, $Cu(NO_3)_2·3H_2O$, $CuSO_4·5H_2O$, $CuCl_2$ and ligands: 1,2-bis(4-pyridil)ethylene (bpe); 1,2-bis(4-pyridil)ethane (bpa); 1,3-bis(4-pyridyl)propane (bpp); 4,4'-bipyridine; 4,4'-azopyridine; 1,4-diazobicyclo[2.2.2]octane (DABCO) and urotropine (hmt). Different metal-organic networks with various topologies and dimensionalities were obtained, depending on the starting Cu(II) salts. All products were synthesized using the same reaction conditions, with 1:1 or 1:2 molar ratios and methanol as solvent.

The chain-like structure of compound ${}^{1}_{\infty}[Cu(bpp)_2(BF_4)_2]$ is depicted in Figure 1. The data obtained from X-ray diffraction reveals a significant influence of the nature of anions on the self-assembly of the coordination frameworks. The anion exchange properties of the obtained coordination polymers are under investigation.

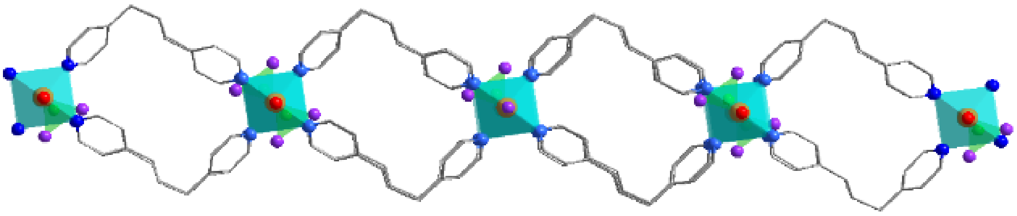

Figure 1. The chain-like structure of compound ${}^{1}_{\infty}[Cu(bpp)_2(BF_4)_2]$

References:

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Synthesis and characterization of a new oxovanadium(V) complexes based on benzaldehyde-derivatives Schiff bases

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Following the condensation of benzaldehyde derivatives, such as salicylaldehyde (sal) and 5-bromosalicylaldehyde (Br-sal) with D or L- valine (D/L-val), we have synthesized two new compounds, each with its D and L enantiomers, respectively.

The molecular formulas of the mononuclear and binuclear oxovanadium(V) complexes are: $[(VO)(Br\text{-}sal\text{-}L\text{-}val)(CH_3O)(CH_3OH)]$ **1**, $[(VO)(Br\text{-}sal\text{-}D\text{-}val)(CH_3OH)(CH_3O)]$ **2**, $[(VO)_2(\mu_2\text{-}O)(sal\text{-}L\text{-}val)_2(H_2O)]$ **3** and $[(VO)_2(\mu_2\text{-}O)(sal\text{-}D\text{-}val)_2(H_2O)]$ **4**. All obtained compounds have been characterized by single-crystal X-ray diffraction, elemental analysis, and spectroscopic (IR, UV-Vis and circular dichroism) measurements. The crystal structure of the compounds revealed distorted octahedral coordination geometry of the vanadium centers. The structures of mononuclear **1** and binuclear **3** complexes are depicted in Figures 1a) and b). The biological activity of these compounds is under evaluation.

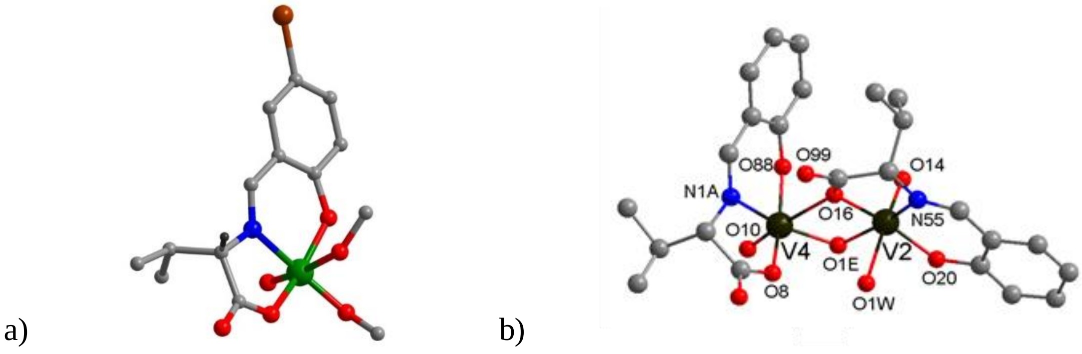

Figure 1. Molecular structure of a) $[(VO)(Br\text{-}sal\text{-}L\text{-}val)(CH_3O)(CH_3OH)]$ and b) $[(VO)_2(\mu_2\text{-}O)(sal\text{-}L\text{-}val)_2(H_2O)]$

In gel determination of α-amylaseactivity

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Enzymes are vital biologicalcatalystswithessentialaction in the metabolism of all living systems.α-Amylase (E.C. 3.2.1.1) is an enzyme that hydrolyses α-glucosidic bonds of large, alpha-linked polysaccharides, such as starch and glycogen, yielding glucose and maltose.[1]. It isthe major form of amylases found in humansandothermammals.[2] It isalsopresent in seedscontainingstarch asnutrientreserve, andit issecretedbymany fungi.

Herein,wereportthein geldetermination of theenzymaticactivity of α-amylasefrom*Aspergillusoryzae*using thepolyacrylamide gel electrophoresistechnique. The methodmakes use ofnative-gel electrophoresis on polyacrylamide gel polymerizedwith0.5%starch. The electrophoreticrunwasperformed at the pH adequatedtotheamylaseactivity.

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Allylic Oxidation of α-Pinene using Cascade Biocatalysis

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Turpentine isthe main waste product ofbulk and paper industry. It is characterised by a low cost price and huge potential in fine chemicals synthesis. Otherwise, turpentine is a natural valuable mixture of terpenoidic compounds. The most known monoterpens of turpentine oil are α/β-pinenes, which are monocycle hydrocarbon with the molecular formula $C_{10}H_{16}$. Pinenes are the main constituents of wood bark and extracted herbal oils. The allylic oxidation of α-pinene drives to the formation of unsaturated compounds, respectively verbenol and verbenone, which are raw materials in flavour and fragrances industries, food and agrochemical sector, phytotherapeutical and medicinal products.

We propose an alternative for α-pinenevalorization based on cascade biocatalytic process. Unspecific peroxidase and laccase cocktail is responsible for catalysing the oxidation of α-pinene leading to verbenol and verbenone mixture. The substrate is allylic oxidised based on peroxidase enzyme followed by transformation of alcohol to ketonic compound in the presence of laccase.

The bi-enzymatic cocktail consists of 2-1B variant peroxidase and M120 laccase with high catalytic activity in aqueous medium. The oxidationreagent is hydrogen peroxide, due to its easy handling, low cost, non-toxicity and the ability to generate water as a by-product. The reaction medium contains 30% acetate buffer for keeping a pH at 5.04 and a proper ionic strength for enzymes catalytic activity. The main idea of using an enzymatic cocktail was to improve the catalytic performances of the developed process (*e.g.*α-pinene conversion and selectivity in verbenol and verbenone). Optimization of the experimental conditions was also considered in order to set up an efficient biocataytic system for α-pinene oxidation.

Finally, the developed biocatalytic system allowed to transform 80%α-pinene with a selectivity of 70% in verbenol and 20% in verbenone under optimum experimental conditions such as 0,63Mα(+)-pinene, 1,28M H_2O_2, 12,97 U/mL 2-1B and 10 mg/mLLaccase M120in acetate buffer (pH=5.04) under stirring (1000 rpm) at 40°C for 24h.

A new fluorescence marker for detection of cell viability

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Fluorescence microscopy is a technique widely used in cell study and many fluorescent stains have been designed for a range of biological molecules. Major examples of fluorescent dyes include the nucleic acidstains (DAPI, Hoechst), the actin fibres stain (phalloidin), stains for detection of intracellular calcium (calcein, Fura-2), etc.

In the present work we studied three fluorescent ligands synthesized in the Department of Inorganic Chemistry for their potential use as (sub)cellularfluorescent stains. We found that in spite of their hydrophobic structure, the compunds tested failed to cross the plasma membrane of live cell, a pre-requisite for vital stains. Nevertheless, one compound crossed the membrane barrier of the dead cells, pinpointing it as a potential fluorescent marker of cell viability.

Pyridine-based [2]rotaxanes designed as switchable catalysts in coupling reactions

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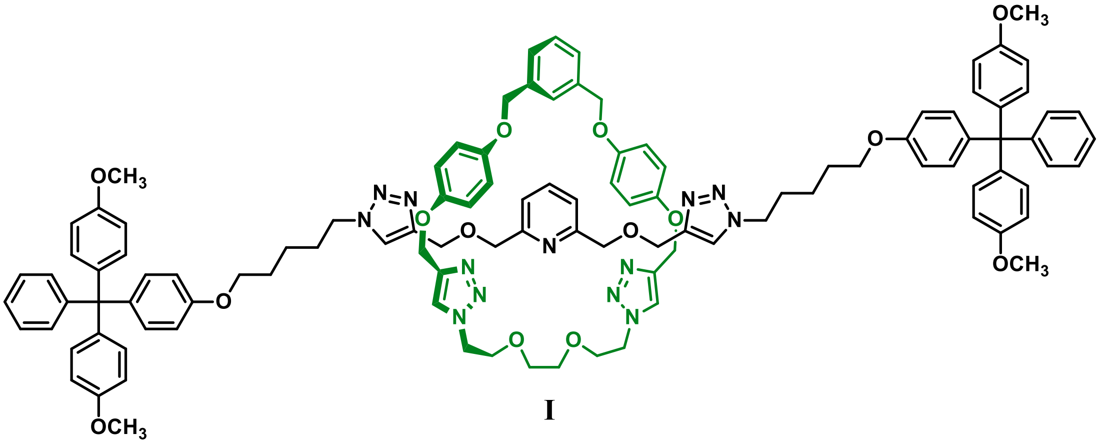
[2]Rotaxanes are supramolecular interlocked architectures consisting of a macrocycle trapped around a dumbbell shaped molecule. In the last years, these compounds found fascinating applications in catalysis. Our goal is to synthesize a [2]rotaxane which will be used as switchable catalyst for cross-coupling reactions.

Herein, we present the synthesis and characterisation of the intermediates for two pyridine-based [2]rotaxanes. Thus, we synthesized the dumbell shaped molecule and precursors for two macrocycles. The first attempts to obtain the target compound **I** (Figure 1), by closing the macrocycle around the axle using a „click” reaction, yielded the expected [2]rotaxane, as inferred by HRMS. The structure and dynamics of **I** are under investigation.



I

Figure 1: Structure of the obtained [2]rotaxane

Degradation of Indigo Carmine Dye in the Presence of Laccase

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Laccase (E.C 1.10.3.2) catalyzes the oxidation of aromatic substrates with the simultaneous reduction of molecular oxygen to water. It has significant potential for use in many applications due to its high reaction rates, broad substrate-specificity, and use of oxygen as an inexpensive cosubstrate. The objective of this study was to investigate the ability of laccase from *Trametes versicolor* to catalyze oxidation of indigo carmine (a widely used food dye) under a variety of reaction conditions. The initial rates of reaction in different conditions were estimated from absorbance *vs.*time curves at 609nm, where the dye has the maximum absorbance.

It was found that the reaction obeys the Michaelis-Menten kinetics and the affinity of laccase for indigo carmine is high, the value of K_M being around 10^{-6}M. The optimum pH of laccase was 4.5; at pH over 6, the reaction is almost negligible. From the variation of initial rates with temperature, the activation energy was estimated (26kJ/mole). In the presence of some mediators laccase was either activated (ferrulic acid, coumaric acid and caffeic acid) or inhibited (quercetin and catechin).

It can be concluded that the degradation of indigo carmine in the presence of laccase is a feasible method for its removal from wastewaters.

Modelling of CO2 absorption process in sodium hydroxide-glycerol aqueous solution using a three-phase fluidized column

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Carbon dioxide capture is one of the most important approaches to reduce the global climate change. Among several CO2 capture methods, absorption perhaps is considered to be one of the most attractive technologies. In order to reduce the energy waste of the absorption process, a solvent soluble in water with a good affinity toward CO2 and a lower heat capacity such as glycerol can be used. Among several possible co-solvents with similar properties, glycerol was chosen due to its increased production as a by-product in the biodiesel industry [1].

This work is focused on modellling and simulating CO2 absorption in aqueous solution of NaOH and glycerol, using a three-phase fluidized column with spherical particles. The fluidized bed regime leads to a process intensification phenomenon due to the continuous renewal of the gas-liquid transfer film. Hence, the highly increased effective transfer surface area. The model was developed according to the experimental data [2] obtained in a lab scale absorption column, in case of CO2 absorption in NaOH aqueous.This validated model was adapted in order to see how the addition of glycerol to the absorbent mixture influences the process. The kinetics model presented in literature by Song and Rochelle was used to calculated overall reaction rate constants for competing effects of CO2/NaOH and CO2/glycerol reactions [3].

After running the model at different values of both gas and liquid flow and also and different concentrations of hydroxide and carbon dioxide and comparing them to the experimental data, the multiple correlation coefficient obtained was R=0.9740.

The conclusion that can be drawn is that the addition of glycerol highly increases the absorption rate.Moreover, the process being conducted in a fluidized bed column, the hydrodynamic caracteristics have a strong impact on how it works. Hence, the absorption rate is influenced by both the fluidized bed height and the fluidization velocity.

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Synthesis and characterization of new Geländer-type macrocycles

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Geländer-type compounds are fascinating molecules with spiral staircase's structures and, therefore, helical chirality. These compounds are very important targets in supramolecular chemistry mainly due their potential applications as stereoselective hosts that allow discrimination of enantiomers as guests.

Herein we report the synthesis and structural characterization of two Geländer-type macrocycles, namely, *p*-terphenyl dietheroxime backbone conected with oligoethilen oxide or 1.3-bis(methylen)arylen chain (Figure 1).

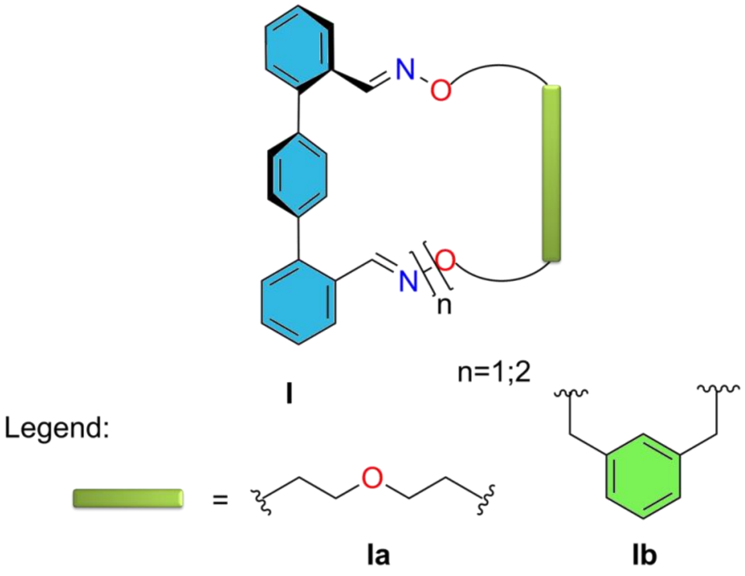

Figure 1: Representation of the target Geländer-type *p*-terphenyle macrocycles

Synthesis and characterization of copper(I) complexes with triphenylphosphine and aroyl thioureas

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Reaction of copper (II) halides (CuX_2, X=Cl, Br) with triphenylphosphine (PPh_3) in ethanol leads to two types of complexes: one tetranuclear $[CuXPPh_3]_4$ and the other one mononuclear with tetrahedral geometry $[CuX(PPh_3)_3]$. These complexes in reaction with aroyl/acyl thioureas (BTU) in toluene leads to tetrahedral complexes $[CuX(PPh_3)_x(BTU)_y]$. Such complexes have been to possess biological activity. Two different complexes have been prepared: 1) x=1, y=2 and 2) x=2, y=1. The structures of these complexes were investigated by ^{1}H, ^{13}C, ^{31}P NMR spectroscopy as well as IR and UV-Vis spectroscopies.

In the initial step three complexes with triphenylphosphine have been prepared: $[CuCl(PPh_3)]_4$, $[CuBr(PPh_3)]_4$ and $[CuBr(PPh_3)_3]$, which were the precursors for four mixed copper(I) complexes with triphenylphosphine and aroyl/acyl thioureas: 1-benzoyl-3-p-tolyl-thiourea (BTU-Me) and 1-benzoyl-3-(4'-methoxyphenyl)-thiourea ($BTU\text{-}OCH_3$) with the following formulae: $[CuBr(PPh_3)_2BTU\text{-}Me]$, $[CuBr(PPh_3)_2BTU\text{-}OCH_3]$, $[CuBrPPh_3(BTU\text{-}Me)_2]$ and $[CuClPPh_3(BTU\text{-}Me)_2]$.

Gas-phase mild amine oxidation on structured carbon-based catalysts

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Nitriles and amides are key intermediates for the production of various value-added products such as materials, agrochemicals, drugs and fine chemicals. Most actual synthesis routes involve toxic or pollutant reagents, therefore, greener synthesis routes like those considering the catalytic mild oxidation of amines by O_2 attracted significant interest. Carbocatalysis offers an interesting sustainable alternative; it is based on the oxidation capabilities of graphene oxyde (GO) entities.

Carbon micromonoliths prepared by carburization of the austenitic stainless steel supports generate a hierarchical structure exposing a graphene layer at the surface [1]. Gas-phase catalytic tests were performed using an *in-house* built experimental setup featuring a tubular flow reactor. Kinetics has been determined for low conversions assuming a mass balance for a continuous stirred tank reactor that allows the direct calculation of the average specific rate of product *i* formation in the conversion range [0, X_i].

Total conversion of the amine was achieved at high temperatures (over $180^{O}C$); at $150^{O}C$ for heptylamine C=50% (F_0 = $4.23 \cdot 10^{-7}$ mol·s^{-1}) and butylamine 50% (F_0 = $8.47 \cdot 10^{-7}$ mol·s^{-1}); at $150^{O}C$ for heptylamine C=5% ($1.7 \cdot 10^{-6}$ mol·s^{-1}) and butylamine 11% ($3.39 \cdot 10^{-6}$ mol·s^{-1}). Besides the reaction conditions the selectivity of the oxidation related to the length of the hydrocarbon as well. Thus, the selectivity in nitrile was higher for heptylamine whereas for butylamine the major oxidation products were *N*-butylidenbutilamine and butanamide. The products distribution determined under differential conditions (low conversion values) allowed kinetic interpretations of the amine oxidation process.

The experiments carried out in this study demonstrate the versatility of the carbocatalysts for selective oxidations.

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Section 2

Mesoporous silica particles as a new support for the immobilization of supramolecular humic acid assemblies

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Introduction: Increasing food production for a growing world population without compromising natural resources for future generations represents one of the greatest challenges for agricultural science. One potential solution to help promoting sustainable intensification in agriculture is the use of plant biostimulants based on humic substances. Our study is part of a research project, which aims to obtain biostimulants for plants, based on the immobilization of humic acids (HA) on mesoporous silica supports.

Results: The prepared amino-silica particles are designed to be able to immobilize *in situ* humic substances, both by bonding them on the particles surface, and also by embedding them inside the particles. Samples of HA - loaded particles (B5 – B8) were compared to a blank sample (B4), synthesized in the absence of HA. For B4 sample, the resulted silica particles were spherical, small and uniform in size (~500 nm). The HA-loaded particles were larger (~ 800 nm) and with a polydisperse size distribution. Beside the modification of particles size, the N_2 adsorption-desorption isotherms are another evidence of the embedding of HA inside the pores of the obtained silica particles. Complete immobilization of HA on the silica support was confirmed by the decrease from 0.9 to 0.04 in UV-Vis absorption spectrum recorded at wavelength 254 nm.

Conclusions: Immobilization of humic acids on mesoporous silica supports was achieved with the prospect of obtaining biostimulants for plants. Optimum results were obtained for a HA concentration of 1.2 g/L, confirmed by various characterization techniques. The group focuses on optimizing the method and further on, adding strigolactones into the system to test the environmental and biological effects over plants growth.

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Ethane oxydehydrogenation over titanium pyrophosphate-supported NiO catalysts

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Ethane oxydehydrogenation (ODH) is an attractive alternative to conventional ethylene production via steam cracking [1]. Supported NiO is a promising catalyst for ethane ODH, its catalytic performance depending on the nature of the support [2]. To the best of our knowledge, titanium pyrophosphate has never been used as a support for NiO.

In this work, five NiO catalysts containing 10, 15, 18, 22 and 26 wt. % of Ni supported on titanium pyrophosphate were studied in ethane ODH. The titanium pyrophosphate support has been prepared by the sol-gel method starting from $TiCl_4$ and H_3PO_4. The solid obtained was poorly crystallized and had a surface area of 107 m^2/g. The supported NiO catalysts were prepared by the wet impregnation of the support with an alcoholic solution containing a precise quantity of nickel nitrate. The impregnated solids were dried over night at 80 °C and then calcined at 450 °C for 5 h. The supported catalysts were labeled as Ni(x)TiP with x = 10, 15, 18, 22 and 26. They were characterized by ICP-OES, XRD, nitrogen adsorption, H_2-TPR and CO_2-TPD and then tested in the ODH of ethane with air at atmospheric pressure in the temperature range from 350 to 450 °C. While the support was not active in the temperature range studied, the activity of the Ni(x)TiP catalysts increased with increasing the Ni content. Compared at isoconversion, the ethylene selectivity also increased with the Ni content, in line with the observed increase of basicity. The best catalyst emerged Ni(26)TiP, which has shown a relatively high ethylene selectivity of 65 % at a conversion of about 50 % at 450°C. This system is comparable or even better than other supported NiO catalysts reported in the literature.

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Synthesis of dia- and para-magnetic polycarboxylic ligands for metal ion complexes

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Employment of polycarboxylic ligands in coordinative chemistry allows generation of impressive structures in the form of metal ion complexes which exhibit interesting properties of importance for many applications. Noteworthy examples for their uses are development of contrast agents for magnetic resonance and optical imaging[1], design of probe/tag pairs for protein labelling[2] or manufacture of materials for protein purification[3]. Stable free radical-derived ligands, have also afforded, in combination with metal ions, structures with interesting magnetic properties.[4]

Herein, we describe the synthesis of a polyaminopolycarboxylic ligand, displaying iminodiacetate moieties, derivatization of the ligand with radical moiety (*e.g.* TEMPO), along with their use in obtaining metal ion complexes with various properties (Figure 1).

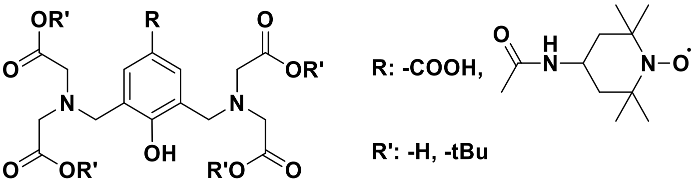

Figure 1. Structures of the polyaminopolycarboxylic derivatives

All synthesized compounds were purified and characterized by different techniques (NMR, UV-Vis, EPR).

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An amino – based Cu(II) metal – organic framework as a highly active basic catalyst for the Henry reaction

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The catalytic testing of a 3D coordination polymer $_\infty[Cu_2(mand)_2(hmt)]\bullet H_2O$ (where mand = totally deprotonated mandelic acid, hmt = hexamethylenetetramine) in the nitroaldol C – C coupling reaction is reported. The catalyst has been prepared by the slow evaporation of a solution containing mand:hmt:Cu^{+2} in a 1:1:1 molar ratio. The obtained MOF was activated by a simple heat treatment, resulting in the elimination of supramolecular water from the 1D channels. The newly exposed uncoordinated amino groups coming from the hmt linker (Figure 1) facilitate the nitroaldol reaction. The activated MOF has been characterized in solid state by PXRD and FT – IR analysis, and its surface area and pore size distribution were obtained from nitrogen adsorption isotherms.

The catalytic tests have been carried out in a glass reactor. The substrates employed in the organic reaction are nitromethane, 1–nitropropane and different aldehydes (benzaldehyde, p–nitrobenzaldehyde, p–bromobenzaldehyde, p–methylbenzaldehyde). After the reaction, the solution has been filtered, evaporated, and then purified by silica gel column chromatography using petroleum ether and ethyl acetate (6:1) as eluent followed by evaporation at room temperature. The recovered products from the liquid phase were analysed and identified by GC-MS and ^1H and ^{13}C NMR spectroscopy.

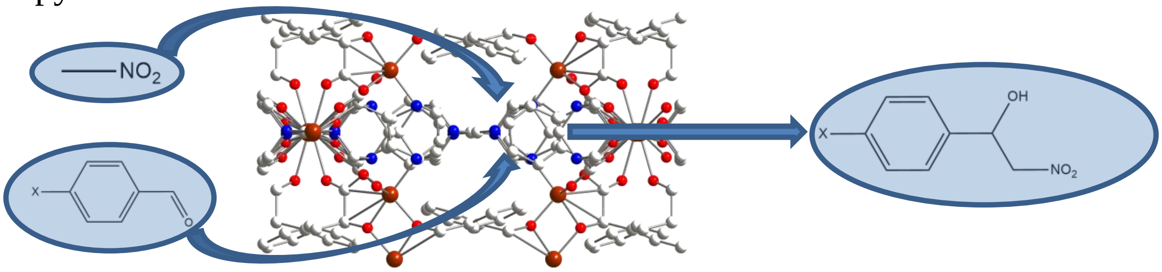

Figure 1. The uncoordinated amino groups (blue) that facilitate the Henry reaction.

Section 3

Novel [$Zn^{II}Ln^{III}$] luminiscent coordination compounds deposited of graphene

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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 complex 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].

Heterometallic[$Zn^{II}Ln^{III}$] complexes containing as ligand a Schiff-base derived from *o*-vanillin have been studied in the past for their luminescent properties, because the ligand acts like an antenna for the lanthanide[2].By using the appropriate lanthanide precursor, it is possible to create a carboxylate bridge between the two metallic ions. Moreover, this carboxylate can be replaced with another one, having different functionality.For instance, the 1-pyrenebutirate was added in the structure, resulting [$Zn^{II}Ln^{III}$] complexes containing a pyrene fragment (where Ln= Nd, Eu, Gd, Tb, Sm, Dy). Having this moiety, the complexes were attached to the graphene surface, where they kept their luminescent properties.

All the compounds have been characterized in solid stateusing FTIR, UV-Vis spectroscopy, luminescence measurements, 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, Raman and luminescence measurements.

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3d and 4f complexes with symmetrical and asymmetrical Mannichbase derivatives

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In coordination chemistry,Mannich reactions together with Schiff reactionsrepresent a facile synthesis pathway toward a rich library of organic molecules with various coordination abilities [1].

Symmetrical ligands are used usually to obtain homo-oligonuclear complexes with 3d or 4f metal ions.Ofhigher interest are asymmetric organic molecules with multiple binding sites due to the possibility to synthesize heterometallic complexes. While examples of 3d-3d' and 3d-4f complexes are numerous,being synthetized for their interesting optical and magnetic properties, examples with two different lanthanide ions are still scarce [2]. The small differences between their properties and ionic radii make the synthesis of f-f' heterodinuclear compounds a difficult task to deal with [3].

The engraftment of paramagnetic species like nitronyl-nitroxide and tempo radicals onto the organic ligand can be converted into heterodispin (2p-3d, 2p-4d, 2p-4f) or heterotrispin(2p-3d-4f) complexes [4].

Hence, several compounds have been synthesized from symmetrical and asymmetrical Mannich base derivatives and 3d or 4f metal ions. The complexes were characterized in solid state using FTIR, UV-Vis spectroscopy, luminescence measurements, powder and single crystal X-ray diffraction, thermogravimetry (TG, DTG, DSC), and EPR spectroscopy. Luminescence properties of complexes with Mannich derivatives of fluorescein were also investigated in solution.

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