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

Students' Scientific Communications Session

- The 17th Edition -

Book of Abstracts - Part 2

May 27-28th, 2022

Bucharest, Romania

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

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Content

Section 1 - MASTER Level

Computational Investigation of Group 6 Metal Carbonyl Derivates with 2-Propanoneoximato and Related Ligands

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Metal carbonyl anions can be used as nucleophiles for reactions with organic halides to synthesize organometallic compounds exhibiting unusual types of metal-ligand bonding. In this connection the reaction of the metal carbonyl anion $CpMo(CO)^{3-}$ (Cp = η^5-C_5H_5) with the nitrosoalkyl halide $Me_2C(NO)Br$ was found to give the purple 2-propanoneoximato complex $(Me_2CNO)Mo(CO)_2Cp$ represented the first example of a metal carbonyl derivative with an oximato ligand obtained by deprotonation of a ketoxime.

A characteristic of compounds with nitrogen-oxygen bonds is their potential oxidizing power owing to the weakness of the nitrogen-oxygen bonds. The reactivity of such oximato metal carbonyl complexes has hardly been explored. In order to explore this essentially unknown aspect of metal carbonyl oximato chemistry as well as the variety of bonding modes of oximato ligands we have used density functional theory to explore the $(Me_2CNO)M(CO)_nCp$ (M = Cr, Mo, W; n = 1, 2, 3) potential energy surfaces with regard to favored structures and thermochemistry

Reference: Th. M. Dănescu, R. Silaghi-Dumitrescu, A. Lupan, R. B. King, *New J. Chem.*, **2021**, *45*, 21092.

The influence of H-bonding on luminescence properties of novel *N*-acylhydrazones

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N-Acylhydrazones have been a highly investigated class of compounds, and implicitly a great number of papers concerning their synthesis and applications in different fields ranging from supramolecular chemistry to material science and bioorganic chemistry1 have been published. In the recent years, the interest has focused on their ability to function as molecular switches. Indeed, *N*-acylhydrazones are well known as photoswitches *i.e.* molecules that can be reversibly converted from one state, or isomer, into another one, by irradiation.2,3 It is well known that *N*-acylhydrazones, when stabilized by intramolecular hydrogen bonding, act as switches by E/Z photoisomerization.4 Consequently, their use as photoswitches provide now an invaluable tool for a large variety of applications in several fields of chemistry, such as organic supramolecular chemistry, materials sciences as well as biology and medicine.2,5,6

Fig 1. Structures of the target *N*-acylhydrazones **1**–**3** and solvatochromism of compound **2a**

Herein we describe the synthesis, structural investigations, and preliminary characterization of the optical and electronical properties of some *N*-acylhydrazones bearing *ortho-* or *para*-hydroxyphenyl groups. The UV-Vis and fluorescence properties in solution and solid-state, the solvent dependent emission behavior as well as the influence of hydrogen bonds on their photochemical properties were investigated. In case of compound **1** (figure 1), X-ray diffraction experiments showed its crystallization with water molecules. Inter- and intramolecular hydrogen bonds observed in the lattice of this compound are most probably responsible for the stabilization of the unexpected *E*-configuration.

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New cobalt (II) and nickel (II) complexes with nicotinamide as potential antimicrobial agents

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Nicotinamide (NA), also known as 3-pyridinecarboxamide or niacinamide, is one of the three components of vitamin B3 and a component of the coenzymes nicotinamide-adenine-dinucleotide (NAD) and nicotinamide-adenine-phosphate (NADP), which are the main electron transporters in many biological redox reaction [1]. Nicotinamide, on the other hand, is known for their biological activities such as antitumor, antimicrobial, antiviral, anticonvulsant, and antidepressant.

Transition metal complexes with nicotinamide have been the subject of some reports having in view their potential biological applications.

Based on these aspects new cobalt (II) and nickel (II) complexes with nicotinamide and acrylate/metacrylate ions as ligands were synthesized. These compounds were characterized by using chemical analysis as well as IR, UV-Vis-NIR spectroscopy and single crystal X-ray diffraction (Fig. 1).

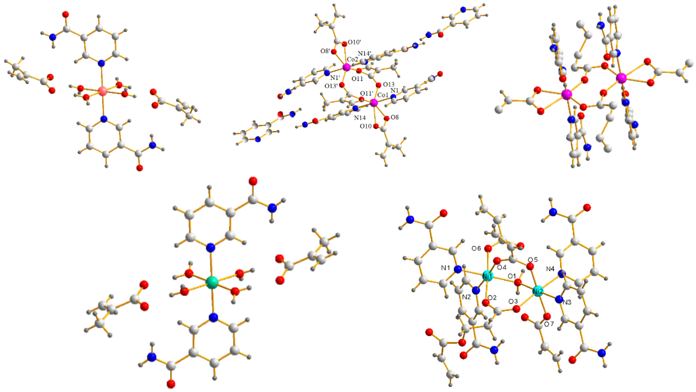

Fig. 1 Molecular structure of complexes

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Study of the electronic properties of $La_{1-x}Sr_xMnO_3$ (x = 0-0.15) perovskites by *in situ* electrical conductivity measurements

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Amongst the many perovskite-based catalysts tested in catalytic combustion reactions, La-Mn-containing systems have shown some of the highest activities in the oxidation of methane.1 In order to gain insight into the involved reaction mechanism, the highly sensitive technique of *in situ* electrical conductivity measurements can be employed to correlate the electronic and redox properties of the catalysts with their performance.2 In this work, a series of $La_{1-x}Sr_xMnO_3$ perovskite catalysts, where $x = 0 – 0.15$, were studied and characterized by means of *in situ* electrical conductivity measurements, which highlighted their semiconductive and redox properties. Their electrical conductivity was first measured as a function of both temperature and oxygen partial pressure, thus establishing the semiconducting character and the nature of the main point defects responsible for the electrical conduction. In addition, the polaron-based conduction mechanism of these manganites was put into evidence. Then, the electrical conductivity of the catalysts was studied with time while successively exposed to air, methane-in-air (reaction mixture) and methane-in-nitrogen mixtures, all under process conditions close to those of catalytic combustion. These sequences allowed the proposal of a potential catalytic oxidation mechanism taking place on the $La_{1-x}Sr_xMnO_3$ catalysts. Furthermore, the effect of the calcination temperature on the electrical properties of the $LaMnO_3$ sample was studied. It has been shown that the increase of the calcination temperature from 600 to 800 °C led to a change of the semiconducting character from *n*-type to *p*-type with consequences in catalysis.

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Zn(II) and Ag(I) complexes with luminescent tripodal ligands

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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 tripodal ligands can act as receptors for different chemical species: transition metal ions, lanthanide ions, anions, or cations and anions in the same time.
A series of mononuclear Ag(I) complexes was obtained using various silver (I) salts and the tripodal ligand derived from 2-fluorenecarboxaldehyde and tris(2-aminoethyl)amine. The second series represents the Zn(II) complexes containing the tripodal ligand derived from 9-anthracenecarboxaldehyde and tris(2-aminoethyl)amine (Figure 1). All the complexes were structurally characterized by X-ray diffraction on single crystal. The optical properties (IR, UV-Vis, luminescence) of the ligands and complexes were analysed in the solid state.

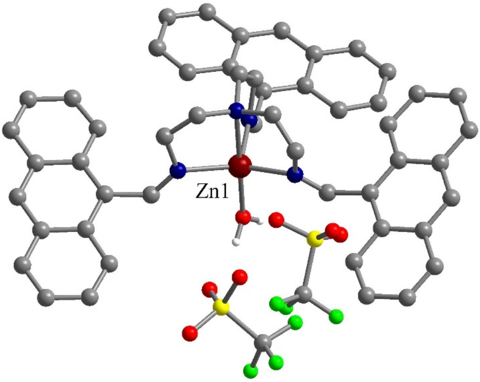

Figure 1. Perspective view of the crystal structure of the complex $[Zn(L^2)(H_2O)](CF_3SO_3)_2$, were L^2 is the Schiff base ligand derived from 9-anthracenecarboxaldehyde and tris(2-aminoethyl)amine. The hydrogen atoms of the organic ligand were omitted for clarity

Rapid voltammetric determination of linezolid using a disposable pencil graphite electrode

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Linezolid (LIN) is a synthetic antimicrobial agent that belongs to the oxazolidinone class, its importance being given by the unique mechanism of action based on the inhibition protein synthesis and its activity against multidrug resistant strain of Gram-positive bacteria [1]. An important analytical tool applied in pharmaceutical analysis is represented by the voltammetric techniques due to the fact that they are simple, fast, cost-effective, versatile and non-destructive, possess good performance characteristics and are suitable for miniaturization.

This study describes the electrochemical behavior and the quantitative determination of LIN by cyclic voltammetry (CV) and square wave voltammetry (SWV), respectively, using a HB pencil graphite electrode (PGE). This is cheap, user-friendly and disposable, constituting a feasible alternative employed in the electroanalysis of pharmaceutical compounds [2]. CV and SWV studies established that the electrode process does not depend on the solution pH. Two anodic peaks were obtained by CV using PGE, one of the irreversible electrode processes being controlled by diffusion and the other by adsorption.

Under optimized conditions SW voltammograms showed a single anodic peak at 0.8 V, characteristic for LIN. Linear relationship between the peak current and the antibiotic concentration was obtained from $2\cdot10^{-6}$ M to $1\cdot10^{-3}$ M. The detection and the quantification limit were calculated as $8.01\cdot10^{-7}$ M and $2.43\cdot10^{-6}$ M, respectively. The accuracy and the precision (intra-day and inter-day) of the SWV method were also evaluated. The developed SWV on PGE method was applied for the quantitative determination of LIN from pharmaceutical formulations, the results being in accordance with the values declared by the manufacturer and obtaining good recoveries.

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Structural diversity in the Cu(II) / 1,3-bis(4-pyridyl)propane system

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Copper coordination polymers have attracted considerable interest as functional materials due to their structural diversities and also to their remarkable properties, including gas storage, catalysis, magnetism, luminescence, electrical conductivity and ion exchange [1-3].
New coordination polymers, $^{1}\infty$[Cu(bpp)2(BF4)2] (**1**), $^{1}\infty$[Cu(bpp)(NH3)2(BF4)2] (**2**), $^{2}\infty$[Cu(bpp)2(CF3SO3)2] (**3**), and $^{1}\infty$\{[Cu2(bpp)2(CF3SO3)2(μ2-OCH3)2](CH3OH)\}+ $^{2}\infty$\{[Cu2(bpp)2(CF3SO3)2 (μ_2-OCH$_3$)$_2$](CH$_3$OH)\} (**4**), have been obtained from the reaction of Copper(II) salts with the divergent, flexible organic ligand 1,3-bis(4-pyridyl)propane (bpp), by slow evaporation method. X-ray diffraction on single crystal, elemental analysis, as well as spectroscopic techniques (FT-IR and UV-Vis) were used to obtain the required data for characterization of the compounds.
The structural diversity of the new compounds depends on the starting Cu(II) salts, conducting to 1-D and 2-D extended structures [4]. Compound **1** is a 1-D linear polymeric chain, compound **2** is a 1-D zigzag polymeric chain, compound **3** is a 2-D grid-like polymer with 2 types of parallelograms, the difference being their orientation (horizontally and vertically) and compound **4** has an interesting and not very common structure in which coexist, as parallel layers, 2-D grid-like structures with 1-D linear coordination polymers. Therefore, we can conclude that the structural diversity of the new compounds depends on the starting Cu(II) salts.

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Triacontahexapeptides Designed as Metal-binding Tags

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Genetically modifying proteins with various peptide tags significantly contributed to protein functional studies, to high and rapid purification of recombinant proteins, or to conferring a target protein new characteristics. In this study we designed two triacontahexapeptide tags with potential metal-binding traits. The peptides had the primary sequence LMEQLEECHQEHEECGPGNGEECEQCHEEHMQLMEL (Seq1) and LMEQLEEMHQEHEECGPGNGEECEQMHEEHMQLMEL (Seq2). Seq2 differed from Seq1 at positions 8 and 26, where cysteine was replaced with methionine. Secondary structure prediction indicated that the two peptides can form a coil-coil motif, with the 12 negatively charged glutamyl residues (E) facing outwards and the four histidyl residues (H) facing the space between the helices. Such a secondary structure would allow E to bind non-specifically any positively charged metal ion, while the four H facing inward would be stabilized by imidazolyl-loving cations, such as Co(II) or the paramagnetic Ni(II).

Using overlapping PCR we introduced artificial DNA sequences encoding Seq1 and Seq2 at the C-terminus of myrGFP (Green Fluorescent Protein bearing a myristoylation sequence) cDNA, and the constructs were further expressed in *Saccharomyces cerevisiae* cells as myrGFP-Seq1/2. The myrGFP casette introduces a myristoylation site, allowing both directional targeting to the inner face of the plasma membrane and monitoring of the intracellular localization of the construct. To estimate and to control the potential toxicity of the constructs, the expression of myrGFP-Seq1/2 was monitored by placing the chimeric DNA under the inducible GAL1 yeast promoter. The constructs were investigated against an array of heavy metals in terms of metabolic changes, growth defects and heavy metal (hyper)accumulation.

It is expected that the triacontahexapeptide tags designed would confer a recombinant protein new traits, depending on the metal targeted. Such tags are promising tools on the way to obtain cell factories for organic-framed magnets or cloneable nanoparticles.

Chiral cobalt(II) complexes based on carboxylato and aminoalcohols ligands

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Introduction: Chirality is a fundamental feature of the living world. The most used synthetic strategy for introducing the chiral information into a metal-ion based network consists of choosing of an enantiomerically pure ligand [1]. In this respect, the usage of lactic acid as chiral precursor is a simple and practical alternative. In addition, carboxylato and aminoalcohols complexes have a wide range of potential applications in materials science, catalysis and molecular magnetism.

Materials and methods: Following this idea, we present herein new Cobalt(II) chiral compounds with different dimensionalities. The complexes were synthesized using cobalt perchlorate (($Co(ClO_4)_2 \cdot 6H_2O$), triethanolamine (H_3tea), lactic acid (lac) and triethylamine (Et_3N) for deprotonation.

Results: Changing the molar ratio between the ligands and metal ions affords discrete compounds (mononuclear or tetranuclear complexes) and monodimensional cobalt(II) coordination polymer with helical topology. Electronic and circular dichroism spectra were also performed according to their relevance for each compound.

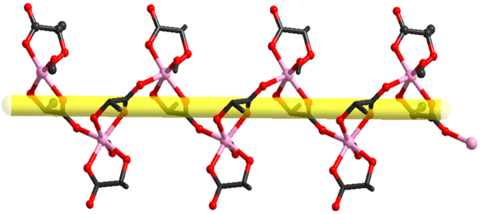

Fig.1 Structure unit in helical cobalt(II) coordination polymer

Conclusions: The crystal structure of the compounds confirm the presence of the Cobalt(II,III) metal ions and homochirality of the complexes. The dichroism spectra suggest the transfer of the chirality from the ligand to metal centers.

Acknowledgements: This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, UEFISCDI, project number PN-III-P1-1.1-TE-2019-1345, within PNCDI III..

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Biologically active complexes of Cu(II) and Zn(II) bearing 1,2,4-triazolo[1,5-*a*]pyrimidine scaffol

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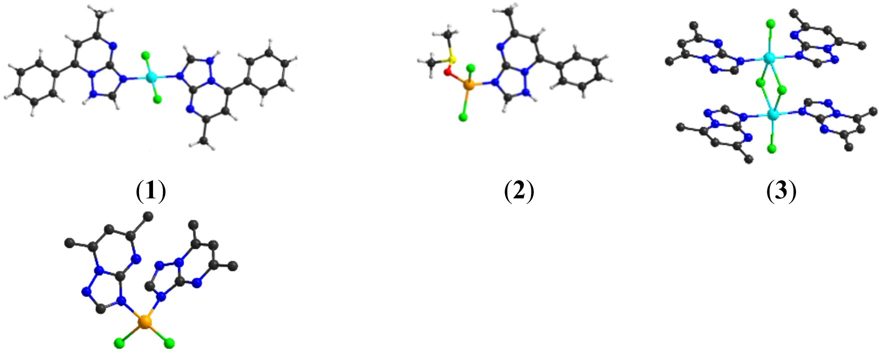
In an attempt to modulate the biological activity of the 1,2,4-triazolo[1,5-a]pyrimidine scaffold through complexation with essential metal ions, the series of complexes *trans*-[Cu(mptp)$_2$Cl$_2$] (**1**), [Zn(mptp)Cl$_2$(DMSO)] (**2**) (mptp: 5-methyl-7-phenyl-1,2,4-triazolo[1,5-*a]*pyrimidine, DMSO: dimethylsulfoxide), [Cu$_2$(dmtp)$_4$Cl$_4$]·2H$_2$O (**3**) and [Zn(dmtp)$_2$Cl$_2$] (**4**) (dmtp: 5,7-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine), were synthesized and characterized as new antimicrobial species. Complexes (**1**), (**2**) and (**4**) contain mononuclear units with a square-planar stereochemistry in the Cu(II) complex and a tetrahedral one in the Zn(II) species. Instead, the structure of (**3**) contains binuclear moieties with Cu(II) in a trigonal bipyramidal surroundings generated through chloride anions that act as bridge. In all complexes the 1,2,4-triazolo[1,5-*a]*pyrimidine scaffold behaves as unidentate ligand through N3 atom (Figure 1). Furthermore, all complexes exhibit an improved antibacterial and antifungal activities compared to the free ligands. Complex (**3**) displays the best antimicrobial activity against Gram-negative (*Klebsiella pneumonia* ATCC 134202, Pseudomonas aeruginosa ATCC 27853), Gram-positive (*Bacillus subtilis* ATCC 6633) and *Candida albicans* 22 microbial strains, both in the planktonic and biofilm-embedded states.



(1) (2) (3)

(4)

Fig. 1. Crystal structure of complexes (**1**) – (**4**) (Cu-blue balls, Zn-orange balls, C-black balls, N-dark blue balls, O-red balls and Cl-green balls)

Section 2 - PhD level

The effect of Mg/Al mol ratio on the catalytic performance of Cu-MgAlO mixed oxide catalysts in hydrodeoxygenation reaction

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Catalytic hydrodeoxygenation (HDO) of pyrolysis oil is considered to be the most effective route to obtain bio-diesel from lignocellulosic biomass.[1] Among the various catalysts studied in the catalytic HDO of oxygen-containing model compounds, Cu-based catalysts obtained from LDH precursors showed promising results.[2]

In this work, a series of Cu-MgAlO mixed oxides with the Cu content fixed at 15 at.% and with different Mg/Al molar ratios, i.e., 1:1, 3:1, 5:1, 1:0 and 0:1, were prepared, characterized and tested in the HDO of benzyl alcohol. Their corresponding precursors were prepared by coprecipitation starting from metallic nitrates using a solution of NaOH 2M as precipitating agent. The obtained precipitates were separated by centrifugation, washed, dried and, finally, calcined at 500 ^{0}C for 5 h to get the mixed oxide catalysts. They were characterized by X-ray diffraction, N_2 adsorption and H_2-TPR. The catalytic tests were carried out in an autoclave reactor at 230 ^{0}C, under 5 atm of H_2 for 3 h

The Mg/Al molar ratio strongly influences the phase, the texture and the reducibility of the Cu-MgAlO catalysts and, hence, their catalytic properties. Consisting of CuO species well dispersed in a Mg(Al)O periclase-like matrix, with good specific surface area and mesopores, the Cu-MgAlO catalyst with Mg/Al = 5 exhibited the best catalytic performances in this series: 97.4 % benzyl alcohol conversion and 87 % toluene selectivity, with benzaldehyde and benzyl benzoate as secondary products.

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Extraction of diclofenac in water samples using supramolecular solvents

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Supramolecular solvents (SUPRAS) are colloid-rich liquids that separate from colloidal solutions under the action of temperature, pH, water or an electrolyte (salt). Supramolecular solvents obtained from reverse micelles resulting from the introduction of alkanols or alkyl carboxylic acids into media containing water and tetrahydrofuran provide regions with different polarities for the solubilization of polar, apolar and amphiphilic analytes which are incorporated resulting in mixed aggregates. At the same time, there is a steric exclusion effect of macromolecular compounds (e.g., proteins, polysaccharides, humic acids, etc.) but also the precipitation of proteins in a matrix with a complex composition [1, 2]. A study on the dosing of diclofenac from wastewater following extraction with such a supramolecular solvent generated *in situ* in the water/1-octanol/tetrahydrofuran (THF) ternary system is proposed. The influence of parameters such as pH and ionic strength on extraction and therefore concentration factor of diclofenac was investigated. Elements related to the development and validation of the HPLC / DAD assay method for diclofenac in water samples are also provided.

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Degradation of multiple organic pollutants from water using a non-thermal plasma-ozonation method

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Water pollution is one of the most important problems of the modern world, especially when considering the progressive reduction of fresh water resources [1]. As such, there is a growing need for advanced water treatment methods capable to remove micropollutants that persist after conventional treatment [2]. In this study, degradation of the contaminants is performed using a plasma-ozonation treatment method [3]. A pulsed corona discharge was generated in oxygen, above the liquid surface. The removal of target pollutants (amoxicillin, ibuprofen, diclofenac) was investigated in mono-, bi- and multi-component solutions having the same theoretical oxygen demand. During treatment, complete removal of all three contaminants is achieved for all solutions investigated. The degradation of the pollutants was accelerated when using the multi-component solution compared to the solutions containing only one or two target contaminants. The mineralization of the pollutants was also higher in the multi-component solution. In order to assess the impact of different salts on the degradation, multi-component solutions were prepared with Na_2SO_4 and $NaHCO_3$. Amoxicillin degradation was achieved faster when using $NaHCO_3$, while Na_2SO_4 improved the removal of diclofenac. Ibuprofen degradation was unaffected by the two salts used. Overall, these results are promising for further application of the plasma-ozonation method.

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Effects of the additive nature and content on the catalytic performance of Nb-NiO in ethane oxydehydrogenation

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The performance of Ni-Nb-O mixed oxide, a promising catalyst for ethane oxydehydrogenation (ODH), was shown to be strongly improved by the addition of small amounts of Co or Ta [1]. Hence, the effect of the addition of Mg, Al, Mn, Fe and Ti, and, for Mg, the effect of its content, on the performance of NiNb mixed oxide catalyst was studied here.

Ni-Nb-O and the ternary M-Ni-Nb-O (M = Al, Mg, Mn, Fe, Ti) mixed oxides with Nb/Ni mol ratio of 0.176 and 10 at.% M or, for M = Mg, within the range 5-20 at.%, were prepared by the evaporation method starting from appropriate amounts of Ni and metal M nitrates (or tetraisopropoxide for M = Ti) and ammonium niobium oxalate, which were added in 200 mL of distilled water (or absolute ethanol for M = Ti). After the evaporation of the solvent at 60 °C and drying, the solids were calcined in air at 450 °C for 5 h. They were characterized by XRD, also applied for the catalysts after the long-term runs, SEM-EDX, XPS, N_2 adsorption/desorption at –196 °C and H_2-TPR, and then they were studied in ethane ODH reaction carried out in a fixed bed down-flow reactor operated at atmospheric pressure, in the temperature range 325-425 °C.

The nature of the cation M = Al, Mg, Mn, Fe or Ti and, for M = Mg, the cation content, strongly influence the physicochemical characteristics and, hence, the catalytic performance of the ternary M-Ni-Nb-O systems leading, for some of them and depending on the reaction conditions, to higher ethane conversion or ethylene selectivity. However, none of the studied additives can prevent the catalyst deactivation on stream, as previously observed for Ta-modified Ni-Nb-O [1].

Acknowledgments

M.M. Trandafir, C. Negrilă and M. Florea from NIMP Măgurele are warmly acknowledged for their help with catalysts characterization.

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Development of a new mild extraction method for the analysis of natural dyes in Cultural Heritage textiles by LC-DAD-MS and gamma radiation's effect

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Abstract

It is well known that identification of dyes provide significant information about biological sources and can thus trace the geographical provenience and historical period of museum textiles. The main problem with flavonoid dyes when it comes to the classical extraction using acid hydrolysis is the decomposition of the glyosidic components to aglycons, resulting in loss of information regarding their biological source. Lately, natural dyes extraction techniques have progressively developed towards milder chemical and physical conditions, in order to preserve the yarn itself and the chromophores[1].

In this present study a new mild extraction procedure with rapid sample preparation and short chromatographic method will be presented, developed in order to preserve glycosides' information and the fibre. This study also describes the effect of gamma radiation on different dyed textiles' experimental models, prepared according to traditional recipes. Irradiation experiments were carried out at about 3.5 kGy/h, with target doses being between 10 and 25 kGy. Aiming to evaluate the versatility of the new extraction procedure, as well as the consequence of using ionizing radiation as decontamination process, this approach was tested on protein materials like silk and wool fibres, dyed with flavones, anthraquinones and indigo. Dyes' characterization and comparison with the acidic extraction was performed using HPLC (High Performance Liquid Chromatography) with diode array (DAD) and mass spectrometry (MS) detection.

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Synthesizing binuclear compounds using compartmental nitronyl-nitroxide paramagnetic ligand

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2,6-dimethylol-*p*-cresol can be oxidized[1] to 2-Hydroxy-3(hydroxymethyl)-5-methylbenzaldehyde (HL^a) and following the adapted[2,3] known[4] procedure the corresponding nitronyl-nitroxide radical (HL) has been synthesized and characterized.[5]

Hence, we report herein the synthesis, structures and properties of two series of dinuclears containing either HL^a, or HL and Ln(III) metal ions, the crystal structure of the impurity encountered during synthesis and the magnetic properties of $[Ln_2L_2(hfac)_4]$, where Ln = Gd, Tb, Dy, hfac = hexafloroacetylacetonate anion (Figure 1). Some of the byproducts were closely investigated and, where it was possible, systematically resynthesized.

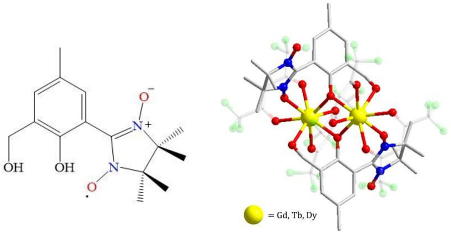

Figure 1. Structure of HL (left) and crystal structure of $[Ln_2L_2(hfac)_4]$ (right).

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