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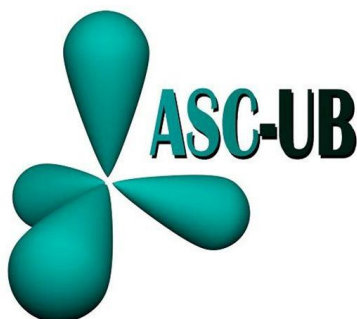
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Section 1

Mn^{II}-Mn^{III} Homometallic Cluster Synthesis and X Ray Crystal Structure

Elena-Daniela Anton, Catalin Maxim, Violeta Tudor, Marius Andruh

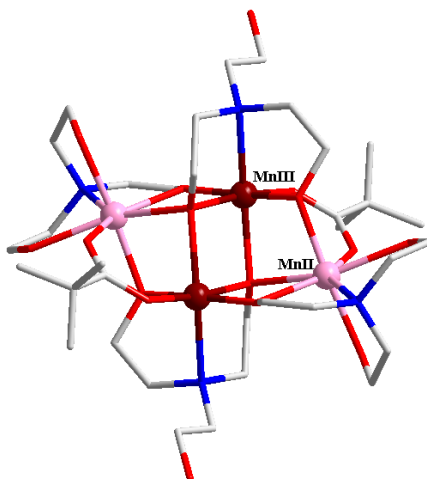
University of Bucharest, Faculty of Chemistry, Department of Inorganic Chemistry, Str. Dumbrova Rosie nr. 23, 020464-Bucharest, Romania

A tetranuclear Mn carboxylate cluster is an integral component of the photosystem II reaction centre of green plants (and cyanobacteria), where it is responsible for the light-driven oxidation of water to dioxygen gas. [1]

Manganese has long been the metal of choice in the synthesis of high nuclearity clusters due to its large numbers of unpaired electrons in the 3d shell (Mn^{II} =d⁵, S=5/2; Mn^{III} =d⁴, S=2; Mn^{IV}= d³, S = 3/2). [2] A new compound containing the common {Mn^{III}₂Mn^{II}₂O₂} ‘butterfly’ core is presented.

The X ray crystal structure of the high-spin tetranuclear cluster [Mn^{III}₂Mn^{II}₂((CH₃)₃CCOO)₂(H₂tea)₂(Htea)₂] (ClO₄)₂ ·2H₂O (1) (where H₃tea = triethanolamine) shows the same coordination sphere and topology of Mn^{II} - Mn^{III} ions as the one reported in [2] but a different out sphere from it.

A new synthesis method is also described.



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2. L. M. Wittick, L. F. Jones, P. Jensen, B. Moubaraki, L. Spiccia, K. J. Berry, K. S. Murray, *Dalton Trans.*, 2006, 1534–1543.

Novel heterometallic clusters Co^{II/III} - Ni^{II}

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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 (H₂dea), Ni(ClO₄)₆·6H₂O and Co(AcO)₂·4H₂O in presence of triethylamine and ethanol afforded two different polynuclear complexes, a heptanuclear complex with formula [Co^{III}₄Ni^{II}₃(dea)₆(AcO)₃]·(ClO₄)₃·2H₂O (**1**) and a tridecanuclear mixed-valent cluster, [Co^{II}₆Co^{III}₄Ni^{II}₃(dea)₈(AcO)₄(OH)₈]·(ClO₄)₃·2H₂O·EtOH(**2**).

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

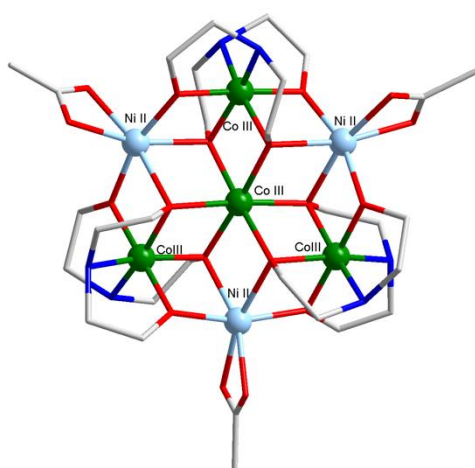


Fig. 1. Structure of compound **1**

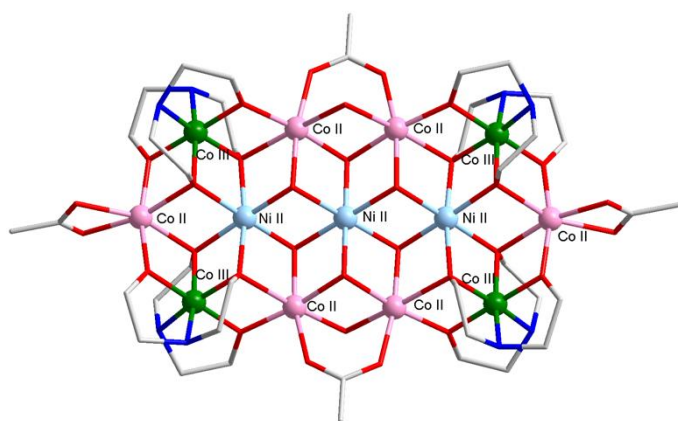


Fig. 2. Structure of compound **2**

¹G. Mezei, C. M. Zaleski, V. L. Pecoraro, *Chem. Rev.*, **2007**, 107, 4933–5003.

The effect of surface phosphorus on the catalytic performance of NiO in ethane oxidative dehydrogenation

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Ethane oxidative dehydrogenation (ODH) is an attractive alternative to conventional ethylene production via steam cracking [1]. NiO-based catalysts are among the most active and selective catalysts for low-temperature ethane ODH to ethylene [1]. On the other hand, it has been shown that modifying oxide catalysts with phosphorus improves their ODH catalytic performances [2].

In this work, the effect of adding phosphorus to bulk NiO surfaces on the catalytic performance of NiO in the low-temperature ethane ODH was investigated and the role of surface phosphorus was unambiguously explained. Thus, surface-phosphated NiO catalysts with different phosphorus contents were prepared and used for ethane ODH in the temperature range from 300 to 425 °C. The catalysts were characterized by nitrogen adsorption at –196 °C, XRD, ICP-OES, Raman spectroscopy and *in situ* electrical conductivity measurements. Adding increasing amounts of phosphorus to NiO changes its physicochemical characteristics; specifically, both the concentration and mobility of the surface lattice O[–] species in the NiO material decrease considerably, affecting its catalytic performance in ethane ODH. Thus, increasing the P content in NiO leads to a decrease in its catalytic activity with an increase in its ODH selectivity at the expense of total oxidation selectivity in the temperature range studied.

Acknowledgments

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

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2. I. T. Trotaș, C. M. Teodorescu, V. I. Pârvulescu, I. C. Marcu, ChemCatChem 5 (2013) 757.

A Family of Coordination Polymers Revealing Kagomé Layers Pillared by Various Ditopic Ligands

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3-D metal-organic frameworks were obtained starting from copper(II) salts, namely $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, and different ditopic organic ligands with N-donors, such as 4,4'-azopyridine (azopy), 4,4'-bipyridyl (bipy), 1,2-bis(4-pyridyl)ethane (bpa), and 1,2-di(4-pyridyl)ethylene (bpe), in aqueous NH_3 at room temperature. Seven coordination polymers of the type $\{[\text{Cu}_3(\text{CO}_3)_2(\text{L})_3](\text{Y})_2\}_n$ [L = azopy, Y = ClO_4^- (1); L = bpe, Y = ClO_4^- (2); L = bpe, Y = BF_4^- (3); L = bpa, Y = ClO_4^- (4); L = bpa, Y = BF_4^- (5); L = bipy, Y = ClO_4^- (6); L = bipy, Y = BF_4^- (7)] have been synthesized.

Spectroscopic techniques, such as FTIR and UV-Vis, single crystal and powder X-ray diffraction, as well as thermal analysis were used to characterize the obtained compounds. The metal-organic frameworks consist of 2-D $\text{Cu}(\text{CO}_3)$ kagomé lattices formed through atmospheric fixation of CO_2 , pillared by the organic linkers, as shown in Figure 1. The gas adsorption properties of these 3-D metal-organic frameworks will be investigated.

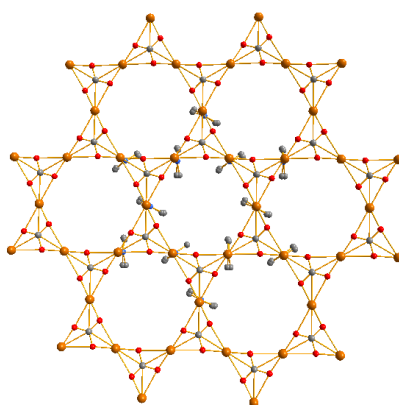


Fig. 1. View of the 2-D kagomé motif in the *ab* plane, where Cu atoms are in brown, C atoms in gray, and O atoms in red (H atoms were omitted for clarity)

Acknowledgements: D.-L. P. & M. A. are thankful to the UEFISCDI for financial support (projects PN-II-RU-PD-2012-3-0528 and PN-II-ID-PCCE-2011-2-0050)

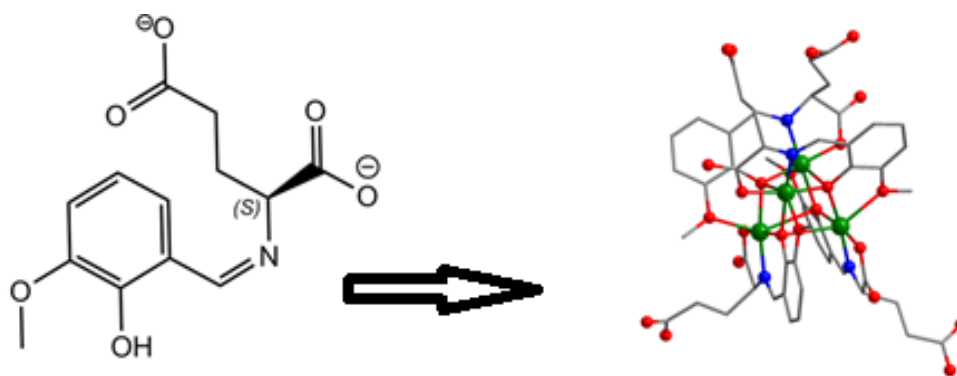
Chiral Cubane-type Cu_4O_4 clusters. Synthesis, structures and chirality

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Enantiopure polynuclear complexes containing multi-metal centres represent a topic of growing interest for synthetic chemists [1]. Chiral magnets have opened up a new field of research on molecular materials which possess both magnetic and optical properties [2].

Our current research is focused on tridentate vaniline-type ligands [3] containing mainly glutamic amino-acid moieties. In this study we present the synthesis and NMR characterisation of new chiral Schiff base ligand containing glutamic acid as a chiral precursor. This ligand was further employed to obtain a chiral cubane type Cu_4O_4 cluster. The physical properties (electronic, fluorescence, CD spectra) have been discussed for each compound.



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Voltammetric determination of propyl-paraben on a pencil graphite electrode

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Parabens are hydroxybenzoic esters. The name “paraben” originates from p-hydroxybenzoic acid^[1]. These compounds are widely used as preservatives in cosmetics. They also possess antimicrobial and antioxidant activity. The antimicrobial activity of parabens increases with an increase in the size of the ester group, which results from the fact that the lipophilicity of these compounds increases in the same direction^[2].

The present paper describes the voltammetric behavior of propyl-paraben (PP) and the quantitative determination of this compound using the pencil graphite electrode (PGE) as working electrode. Due to its good properties as electrode material and its economic advantages (disposable, cheap and easily commercially available) the PGE was largely applied in the voltammetric determination of different compounds^[3].

Cyclic voltammetric studies demonstrated that PP is irreversibly oxidized at the PGE and involves a diffusion-controlled and pH-dependent electrode process which implies an equal number of protons and electrons. For quantitative determinations the more sensitive differential pulse voltammetry (DPV) method was employed. The influence of several chemical (nature of electrode material, nature of supporting electrolyte and solution pH) and instrumental (pulse amplitude and step potential) parameters on the voltammetric response of PP was also investigated. Under the optimized conditions, PP can be determined quantitatively by DPV in the concentration range 6×10^{-7} - 9.6×10^{-4} M presenting two linear ranges: 6×10^{-7} - 1.2×10^{-4} M and 1.2×10^{-4} - 9.6×10^{-4} M described by the following equations $I_p = 190816C - 0.068$ ($R^2 = 0.9998$) and $I_p = 68373C + 17,663$ ($R^2 = 0.9751$), respectively.

1. http://www.medscape.com/viewarticle/508430_2

2. Angelov T, Vlasenko A, Tashkov W (2008) HPLC determination of pKa of parabens and investigation on their lipophilicity parameters. *J Liq Chromatogr Relat Technol* 31:188–197.

3. David IG, Florea MA, Crăcea OG, Popa DE, Buleandră M, Iorgulescu EE, David V, Badea IA, Ciucu AA (2015) Voltammetric determination of B₁ and B₆ vitamins on a pencil graphite electrode. *Chem Pap* 69:901-910.

Synthesis of *O*-decorated phenol functional compounds

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Compounds bearing multiple functional groups found great applicability in organic synthesis, especially in the field of heterocyclic chemistry.¹ Usually, in order to avoid chemoselectivity issues in their specific reactions,² protection of one or more functional groups is required. In addition, presence of convenient groups such as the hydroxyl group may provide the possibility to graft on the target skeleton various substituents that improve the properties of the final product.³

In this paper, we describe synthesis of some substituted *O*-decorated phenols (Figure 1) as intermediates in multi-step organic synthesis of compounds with various applications. Thus, we present synthesis of functional derivatives that contain either easily removable protecting groups or are decorated with moieties able to provide increased solubility in water or organic solvents.

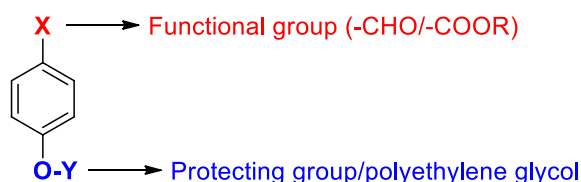


Figure 1 General structure of the synthesized compounds

All synthesized compounds were purified and characterized by spectral analysis (¹H NMR).

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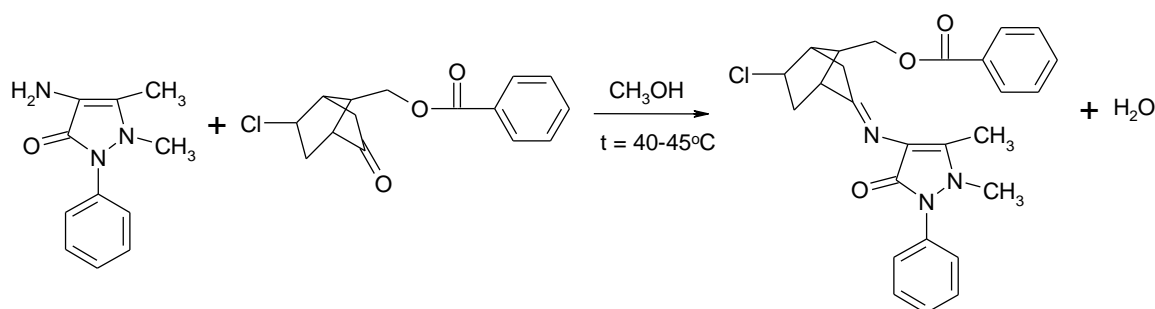
Synthesis and electrochemical behavior of new derivatives from 4-Aminoantipyrine

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4-Aminoantipyrine (4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one, 4-AAP) is a metabolite of aminopyrine with analgesic, anti-inflammatory and antipyretic properties. It can be used as a drug and also as a reagent for biochemical reactions producing peroxides or phenols. 4-AAP stimulates liver microsomes and can be useful to measure extracellular water.

A new compound (base Schiff) derived from 4-aminoantipyrine and 2-keto-5-chloro-7-benzoyloxymethylenebicyclo[2.2.1]heptane have been prepared and characterized. The new compound was synthesized (Scheme 1) and characterized by appropriate means.



Scheme 1. Reaction of synthesis

Electrochemical methods are capable for assaying the concentration of electroactive analyte at trace level and can provide useful information concerning its physical and chemical properties such as oxidation potential, diffusion coefficients, electron transfer rates and electron transfer number.

In this work, redox behavior of the obtained compounds is followed by using cyclic voltammetry (CV) and differential pulse voltammetry (DPV).

Comparison between various oxidation processes of alkenes

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As the Earth is constantly changing, the public awareness of environmental concerns is increasing rapidly. Nowadays, the main priority of every scientist from all over the world is finding innovative solutions to stop or, at least, to decrease the pollution occurred especially in the chemical industry. And there is nowhere a higher demand for “green” catalytic alternatives reagents than in selective oxidation reactions.¹

Herein, we comparatively describe different oxidation methods of alkenes based on Payne and Mukaiyama’s work combining environmentally friendly oxidation agents (H_2O_2 or O_2) with co-reagents such as nitrile or aldehyde² and different solid base catalysts derived from hydrotalcite like compounds, characterized by basicity determination³ in order to obtain a selective conversion of olefins to the corresponding epoxide products.

1. Roger A. Sheldon, Isabel Arends, Ulf Hnefeld, Green Chemistry and Catalysis 2007, Wiley, 18.

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3. Damien P. Debecker, Eric M. Gaigneaux, Guido Busca, Chem. Eur. J. 2009, 15, 3920 – 3935.

Synthesis of key intermediates for preparation of polyaminopolycarboxylic compounds

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Polyaminopolycarboxylic compounds found use as versatile chelating agents, for instance in imaging applications, through their ability to generate near-infrared luminescent complexes with lanthanide ions.¹ In addition, pyridine-based polyaminocarboxylic ligands could be used as tags for specific and selective activity-based protein labelling² or as phasing agents for X-ray crystallography of proteins in combination with lanthanides.³

Herein we describe synthesis of some precursors in the preparation of polyaminopolycarboxylic derivatives containing the iminodiacetic acid moiety (Figure 1). Different synthetic strategies of the intermediates were approached in order to optimize the procedural pathway.

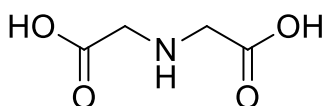


Figure 2 Iminodiacetic acid

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

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3. R.Talon, L.Nauton, J.-L.Canet, R Kahn, E.Girard, A.Gautier, *Chem. Commun.* 2012, 48, 11886–11888.

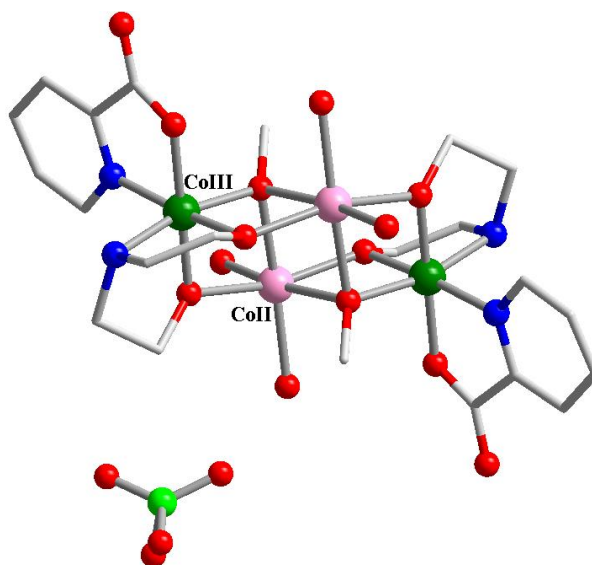
Mixed-Valent Cobalt Tetranuclear Cluster

Cornelia-Lăcrămioara Stoica, Cătălin Maxim, Violeta Tudor,
Marius Andruh

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Tetranuclearity can be considered a common and representative class of high-nuclearity 3d-metal clusters showing interesting properties spanning from catalysis, and magnetism to modeling biochemical reactions. Various coordination motifs have been described in the literature in which the M_4 cores present linear, cubane, butterfly, adamantane, basket, squares, and metallacrown topologies. Cubane-like clusters, found a variety of transition metal complexes, exhibit interesting magnetic exchange properties and under certain circumstances act as single molecule magnets.^[1]

Reactions of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with diethanolamine (H_2dea) and picolinic acid in the presence of triethylamine and methanol afforded a new homometallic tetranuclear complex $[\text{Co}^{\text{II}}_2\text{Co}^{\text{III}}_2(\text{dea})_2(\text{pic})_2(\text{OCH}_3)_2(\text{H}_2\text{O})_2] \cdot 2\text{ClO}_4$. The compound has been analysed by IR and UV-VIS spectroscopy and the crystal structure was determined by single-crystal X-ray diffraction. The Co^{II} and Co^{III} ions, connected by alkoxo and metoxo groups, are in a distorted octahedral geometry. Picolinic acid anions complete the coordination of peripheral Co^{III} ions in a chelatic mode. Two water molecules are coordinated at each central Co^{II} . Diethanolamine acts as tridentate ligand, with the nitrogen atoms coordinated at peripheral Co^{III} and deprotonated alkoxo groups bridging Co^{III} and Co^{II} .



I.S.R.Hosseiniian, V. Tangoulis, M. Menelaou, C. P. Raptopoulou, V. Psycharis, C. Dendrinou-Samara, Dalton Trans, **2013**, 42, 5355.

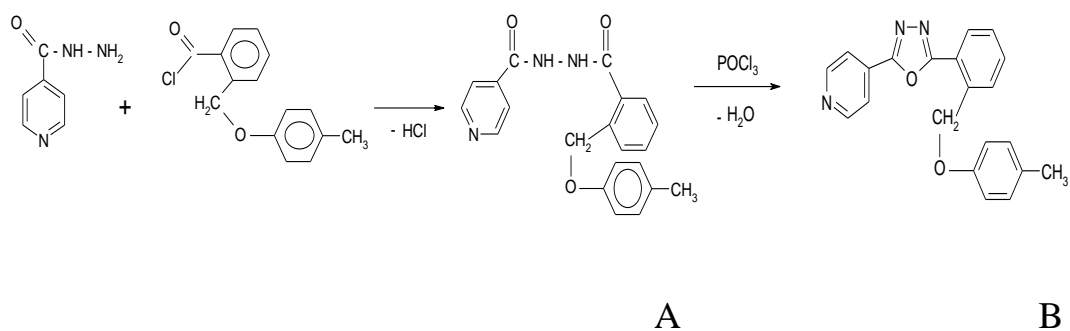
Synthesis and redox investigations of new derivatives of isoniazid

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030018, Bucharest, Romania*

Isoniazid (4-pyridine-carboxylic acid hydrazide or isonicotinic acid hydrazide) is a widely used drug alone in the prophylaxis and in combination with other anti-tuberculosis drugs in the treatment of all forms of tuberculosis.

In this work we synthesized two derivatives of isoniazid (A and B).



The method of synthesis and characterization by appropriate means of 2-(4-substituted-phenoxy)methyl)-benzoic acids were presented. The new heterocycle compound was synthesized and characterized by IR and NMR methods. The electrochemical behavior of these compounds was performed by using two methods: cyclic voltammetry (CV) and differential pulse voltammetry (DPV). CV is one of the first techniques performed in an electrochemical study. It is based on potential control and is used for acquiring qualitative information about electrochemical reactions. It is one of the most versatile electroanalytical tools for the analysis of pharmaceuticals and biologically active compounds.

Section 2

Polynuclear complexes obtained with aromatic hydroxydicarboxylic ligand

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The polycarboxylate aromatic ligands had made in the past decades an amazing research field in the complexes synthesis, with great and very useful results, such as MOFs, SMMs, and many others.^{1,2}In the case of this research we synthesized 5-methyl-2-hydroxy-isophthalic acid starting from 2,6-bishydroxymethyl-*p*-cresol using a two-step oxidation route. This aromatic acid is derived from isophthalic acid, but it brings additional coordination abilities because of its ability to act as a bicompartamental ligand for 3d metal ions, and also creating a high oxygen donor atoms density, which are great advantage for interacting with oxophilic metal ions, such as lanthanides ions.

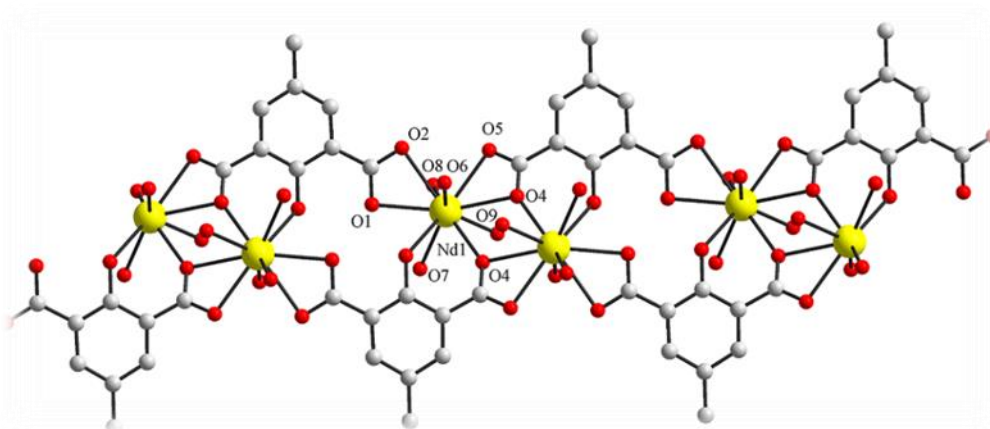


Figure 1-Structure of $[[\text{NdHL}(\text{H}_2\text{O})_4](\text{NO}_3)\cdot\text{H}_2\text{O}]_n$

Using this new ligand we synthesized two new compounds of copper Cu^{2+} , $[\text{Cu}_6\text{L}_4\text{py}_{10}]_n$, and neodymium Nd^{3+} $[[\text{NdHL}(\text{H}_2\text{O})_4](\text{NO}_3)\cdot\text{H}_2\text{O}]_n$ (Figure 1). These compounds are 1D coordination polymers formed by single/polynuclear monomer units.

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The Fine Balance of Ligand Field Factors for Spin Cross-Over Processes in d^6 vs. d^4 complexes

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The spin cross-over (SCO) is fascinating as a phenomenon taking effectively place at the ionic core of several classes of complexes, driven by factors of immediate environment (ligand field), next neighbor arrangements (supramolecular level), as well as from inner atomic structure (the spin-orbit coupling). We compare Fe(II)^[1] and Mn(III)^[2-3] SCO systems, considering that, in the HS state, the d^6 and d^4 are complementary, acting as particle vs. hole companions, with 5D ground term. The Fe(II) gives the most frequent encounters of the SCO phenomena, while the Mn(III) are the most rare SCO cases. With structures from literature reports,^[1,3] we performed the time dependent (TD) DFT calculations, which are usually good for description of charge transfer processes, showing certain limitation in the account of the ligand-field $d-d$ spectra. In this perspective, the considered systems are analyzed, offering an intuitive discussion about the parameters driving the HS-LS balance. We considered such systems as study case for the electronic structure considerations. The difference density maps are used to characterize the nature of the transitions.

Acknowledgement: This work is supported by the PNII UEFISCDI PCCE 9/2010, UB/2014 and ECOSTBIO COST 1305 action.

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Polynuclear Compounds derived from Triphenyltin(IV) Building-Blocks and 1,3,5-Benzenetricarboxylic Acid

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A series of new polynuclear complexes with triphenyltin(IV) nodes and deprotonated 1,3,5-benzenetricarboxylic acid (trimesic acid, H₃tma) as organic linker have been synthesized. All compounds were obtained as colorless single crystals and characterized in solid state by FTIR spectroscopy, elemental analysis, thermal stability, as well as single crystal and powder X-ray diffraction.

Complex $[\{\text{Ph}_3\text{Sn}(4\text{-nitrobenzylpy})\}_2(\mu_3\text{-tma})\{\text{Ph}_3\text{Sn}(\text{CH}_3\text{OH})\}]$, 1, is a trinuclear compound comprising three atoms of tin(IV) bridged by trimesate anion as a tridentate ligand. In the hexanuclear $[\{(\text{Ph}_3\text{Sn}(\text{CH}_3\text{OH}))_2(\mu_3\text{-tma})(\text{Ph}_3\text{Sn})(\mu_2\text{-L})\}]$ complexes, where L = 1,2-bis(4-pyridyl)ethylene (bpe), 2, and 1,2-bis(4-pyridyl)ethane (bpa), 3, two trinuclear organotin nodes formed with the trimesate anion are linked by a diamine molecule. Complex 2 is shown in Figure 1.

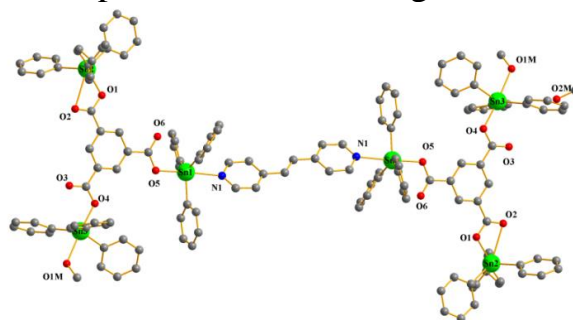


Fig. 1. Molecular structure of $[\{(\text{Ph}_3\text{SnX})_3(\mu_3\text{-tma})\}_2(\mu\text{-bpe})]$
(Hydrogen atoms were omitted for clarity)

Compound 4 is a 1-D coordination polymer with a zigzag chain formed by coordination of trimesate anion, completely deprotonated, to Sn(IV) atoms. 4-Aminopyridine connects two chains through π - π staking and intramolecular hydrogen interactions stabilizing this compound. The biologic potential of all compounds is under investigation.

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Synthesis and Structural Analysis of Simple Homoleptic Lanthanide Complexes

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The magnetic anisotropy is the basic ingredient that determines the formation of magnetization axis that drives a spin-carrier molecule into a nominal magnet. The attention on Single Molecule Magnet class was progressively shifted towards smaller species such as binuclear or even mononuclears, namely Single Ion Magnet cases. The molecular simplicity allows insight into structure-property relationships. In this spirit, we deliberately consider simple mononuclear unit, the $[\text{Ln}(\text{NO}_3)_5]^{2-}$ units (Ln=Sm, Eu, Gd, Tb, Dy, Ho, Er) from a newly synthesized series of systems having complex counterions, $[\text{M}(\text{phen})_3]^{2+}$ (M=Ni, Co). The calculation of lanthanide complexes faces the special problem of the *non-aufbau* nature of the *f* shell in the complex and the weakly interacting nature of the *f* electrons. With the help of computational tools we are able to analyse and even predict the magnetic properties of the units, the presented systems being clear examples.

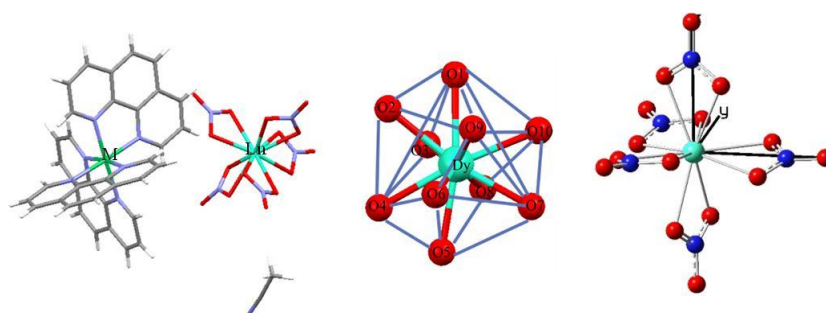


Fig.1. X-ray structure of single crystal $[\text{M}(\text{phen})_3][\text{Ln}(\text{NO}_3)_5]$ (Ln=Gd, Tb, Dy, Ho, Er)(left), coordination polyhedra (center) and geometry pattern (right) of the $[\text{Ln}(\text{NO}_3)_5]^{2-}$ units (Ln=Gd, Tb, Dy, Ho, Er).

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Fe-Mn mixed oxides for *p*-xylene selective oxidation

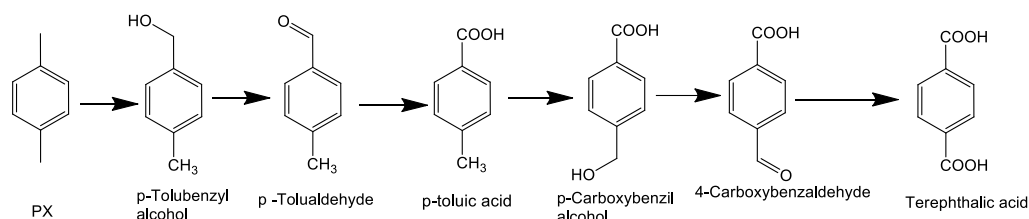
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One of the most valuable carboxylic acid, terephthalic acid (TPA), is produced at industrial scale by oxidation of *p*-xylene (PX) in a homogeneous route using Co and Mn salts as catalysts, known as AMOCO process (Scheme 1). Despite the good results (98% conversion with almost 95% selectivity for TPA) this process is highly polluting and not ecofriendly^[1]. Therefore, new ways for TPA production should be developed.

In this study, mixed oxides catalysts based on iron and manganese, were prepared by two different methods (hydrothermal treatment and citrate method) and were tested in heterogeneous catalytic oxidation reaction of PX. The catalytic materials were characterized by different techniques (BET, TG-DTA, XRD). Catalytic tests were performed in batch reactor, under temperature and stirring, varying reaction parameters in order to find the best formulation.

Catalytic tests showed good activity for both mixed oxides. For Mn/Fe/O catalysts prepared by citrate method total conversion of PX with 80% selectivity for *p*-toluic acid in H₂O solvent and H₂O₂ as oxidant, was observed. Also, oxidation of PX in CH₃CN (solvent) with TBHP as oxidant resulted in a conversion of 63% with selectivity in *p*-toluic acid of 60% for the same catalyst. Changing the preparation method (hydrothermal treatment) we obtained *p*-toluic acid (43% selectivity with 53% conversion of PX) in the presence of similar conditions (CH₃CN solvent and TBHP as oxidant). Different reaction conditions, H₂O solvent and H₂O₂ as oxidant gave 34% conversion with high selectivity (85%) in *p*-tolualdehyde.



Scheme 1

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Synthesis and Structural Analysis of New Pyrazole Copper Complexes

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The oligo- and polynuclear complexes with a special topologies offer case studies on electronic structure magnetic properties. In this work we report the synthesis and structural analysis of some new polynuclear copper complexes based on 3,5-dimethyl-4-nitropyrazole (L1) and 3,5-dimethyl-4-iodopyrazole (L2). Depending on pyrazole derivatives and the anion type we obtained a structural variety on copper polynuclear complexes like chains with formula $[(L1)CuBr]_{\infty}$ and $[(L1)_2CuBr_2]$ and (μ_4 -oxo)-tetranuclear structure. The newly synthesized compound $[(L1)_2CuBr_2]$ crystallizes in the monoclinic system, with space group $P2_1/c(\#14)$ with the following cell parameters $a=3.9769(1)$ Å, $b = 16.556(1)$ Å, $c=12.6933(8)$ Å, $\beta = 96.525(7)^{\circ}$, $V=830.31(8)$ Å³, $Z=2$, $R=0.09$, $F=1.093$. The ligands are oriented reciprocally in trans position in a pseudo planar arrangement. The packing shows a polynuclear chain with long Cu-Br bridges. Selecting the $[Cu_4(\mu_4-O)(\mu-Br)_6(L2)_6]$, the ligand field spectrum and spin states due to intercenter coupling were considered, in the frame of DFT. The system has S_4 symmetry, effectively very close to the T_d point group. The ligand field and charge transfer states were accounted by TD-DFT calculations.^[1] The spin coupling was treated by Broken-Symmetry DFT methodology,^[2] revealing a ferromagnetic situation. The situation is in line with the experimental pattern of magnetic susceptibility curve, where at low temperature there is detected the role of intercenter-dipolar coupling, aside the intermolecular field of weak antiferromagnetic nature.

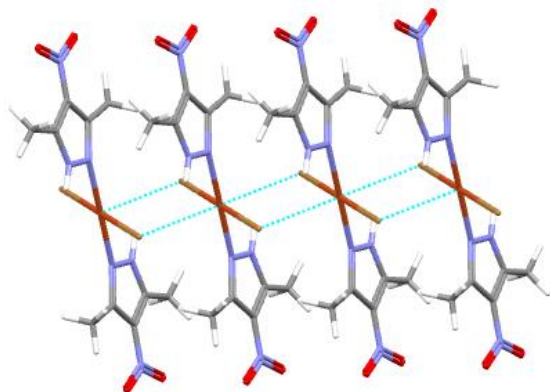


Figure 1. The molecular structures of $[(L1)_2CuBr_2]$

Acknowledgement: This work is supported by the PNII UEFISCDI PCCE 9/2010, UB/2014 and ECOSTBIO COST 1305 action

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Fluoromanganese (III) Chain Complex. Synthesis and Structural Analysis

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To study the exchange interaction via hydrogen bonds we design low-dimensional system with $[\text{HF}_2]^-$ bridges. Such chain structure with interesting magnetic properties are favored by Jahn-Teller stabilization in Mn(III) fluorine compounds with d^4 configuration. 1D- $[\text{Mn}(\text{phen})\text{F}_2(\text{HF}_2)]$ complex, where phen=1,10 phenanthroline, has been prepared from manganese(III) salts and $[\text{Ph}_4\text{P}][\text{HF}_2]$ as fluorinating agent, avoiding to use HF which require special laboratory technique. The crystal structure was determined by single-crystal X-ray analysis: monoclinic, space group $\text{P}21/\text{c}(\#14)$, $Z=4$, $a=8.41510(10)$, $b=7.38090(10)$, $c=19.4205(5)\text{\AA}$, $\beta=102.1159(12)^\circ$, $R=0.070$, $\text{GOF}=1.008$. The structure consists of zig-zag chains where $[\text{Mn}(\text{phen})\text{F}_2]$ units are bridged by $[\text{HF}_2]^-$ anions. The resulting $[\text{Mn}_2\text{F}_4]$ octahedra are strongly elongated. The geometry of the centrosymmetrical bifluoride anion is close to that of KHF_2 (H-F: 1.14 \AA), the angles at the angular bridge Mn-F-H are 119.10° . The packing of the Mn(III) complex molecules shows strong hydrogen bonds along the chain and π - π interaction between the chains (Figure 1).

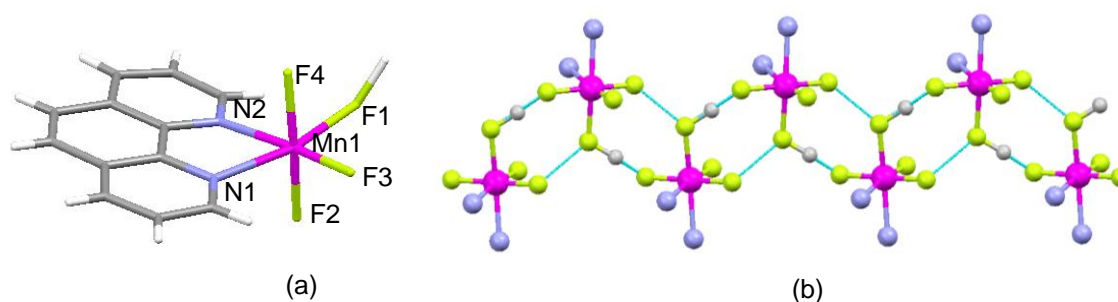


Figure 1. X-ray structure of single crystal $[\text{M}(\text{phen})\text{F}_2(\text{HF}_2)]$ (a)(left), packing detail along the chain (b).

Acknowledgement: This work is supported by the PNII UEFISCDI PCCE 9/2010, UB/2014 and ECOSTBIO COST 1305 action.

Section 3

Organometallic and tetrahedral spacers – new tectons in crystal engineering and metallosupramolecular chemistry

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The employment of divergent ligands and homobinuclear complexes as building-blocks led to interesting coordination polymers with various network topologies and dimensionality following the ‘node and spacer’ approach.¹ The employment of organometallic compounds containing functional groups capable to coordinate to metal ions as spacers is rarely used in constructing coordination polymers. We have demonstrated the ability of bis-pyridyl-mercury to function as tecton in designing coordination polymers and co-crystallization products; the presence of mercury atoms enabling the engagement of the organometallic spacer into non-covalent contacts that extend the molecular assembling into the three dimensions.² To prevail the involvement of the metal atom into supramolecular interactions and the interpenetration phenomenon of networks, we have chosen three new organometallic spacers based on antimony or bismuth and nicotinate and isonicotinate moieties to synthesize and characterize three new coordination polymers.

Tetra substituted adamantane derivatives are useful tectons in generating robust porous structures showing high connectivity topologies. Two rigid tetrahedral organic linkers with adamantane cores have been employed in obtaining a 3-D 4-fold interpenetrated framework featuring a PtS network topology $[\text{CuL}_1(\text{H}_2\text{O})_2](\text{BF}_4)_2 \cdot x\text{H}_2\text{O}$ (1) ($\text{L}_1 = 1,3,5,7$ -tetrakis{4-(4-pyridyl)phenyl}adamantane) and a 2-fold interpenetrated grid-like coordination polymer $[\text{Mn}(\text{hfac})_2(\text{L}_2)_{0.5}]$ (2) ($\text{L}_2 = 1,3,5,7$ -tetrakis(4-cyano-phenyl)adamantane).

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Selective hydrogenation of 4-nitrostyrene over noble metals based catalysts supported on covalent-organic frameworks

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Selective hydrogenation of unsaturated compounds is very important in the production of fine chemicals. Moreover, selective reduction of the C=C double bond in the presence of the other reducible groups like nitro or carboxyl is often required in multi-step organic synthesis¹, but it can be a scientific and technological challenge. A suitable technique for addition of molecular hydrogen to unsaturated compounds is the heterogeneous catalytic hydrogenation, where the generation of wastes is lower compared to the conventional non-catalytic processes.

Covalent-organic frameworks (COFs) are interesting materials which can be potentially supports for metal based catalysts in heterogeneous processes. COFs are synthesized from organic monomers linked together by strong covalent bonds multidentate organic bridging ligands. They have crystalline or amorphous structure with high porosity and low crystal density².

The goal of our study is to selectively hydrogenate C=C in the presence of other reducible groups. The novelty of this research consists in the use of a COF with high surface area and with well-defined and predictable pore structures as support for noble metals. 0.5% Au/COF and 0.5% Pd/COF materials were prepared by deposition-precipitation method in order to be tested in the selective hydrogenation of 4-nitrostyrene.

The catalysts were characterized using the following techniques: Adsorption-desorption isotherms at 77K, TG-DTA and XRD. The high surface area of the COF (774 m²/g) was suitable for good dispersion of the active metal phase. Au and Pd nanoparticles were formed on the surface of the COF as it was illustrated by X-ray diffraction. The hydrogenation reactions of 4-nitrostyrene occurred with a good conversion of the substrate (60-100%) and with high selectivity (100%) for the ethylnitrostyrene (EN).

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