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| **Programul:** | **IDEI** |
| **Tipul proiectului:** | **Exploratory Research Projects** |
| **Cod proiect:** | **PCE\_2012-4-0261** |
| **Nr. contract** | **53/02.09.2013** |
| **Denumirea proiectului:** | **New coordination networks containing polyfunctional flexible bridges** |

**SCIENTIFIC REPORT**

**2016**

**Objectives:**

1. **Preparation of the extended networks based on pre-formed or *in situ* formed metal clusters and the obtained ligands** 
   1. Preparation of the extended networks based on flexible ligands and different metallic precursors.
   2. Determining the chemical and structural composition of the obtained metal complexes by using physical methods of analysis: elemental analysis, TGA, FTIR (MIR/FIR), EDXRF, XRD.
   3. Selection of the interest structures and their investigation by SEM, TEM, AFM to evaluate the morphology and porosity; study of the surface properties by DVS.
2. **Evaluation of some properties and potential applications for the obtained metallo-silicon networks**

2.1. Testing of the networks in hosting various guest molecules acting as storage, separation, catalysis, etc.

**Expected results:**

**🗹*At least a novel network containing metallic clusters and flexible bridges*** – ***achieved objective***

***New networks based on flexible ligands and different metal precursors have been obtained*** whose structure was confirmed by physical methods of analysis: elemental analysis, TGA, FTIR (MIR / FIR), EDXRF and by single-crystal X-ray diffraction. For the structures of interest the morphology (AFM, SEM and TEM) and porosity (from sorption/desorption isotherms of H2 and N2) and surface properties (sorption/desorption isotherms of water vapor-DVS) were assessed.

**🗹*The results of at least an applicability test for three networks*** - ***achieved objective***

For the structures of interest achieved in the project (extended networks containing metal or those based on pre-formed or *in situ* formed metallic clusters and various obtained ligands) were evaluated some properties and potential applications in areas such as catalysis, antimicrobial activity, fluorescence, magnetism. Also it was estimated their theoretical and practical utilization in hosting various guest molecules (N2, H2, CO2, water vapor, etc).

**🗹*At least one presentation at scientific meetings***- ***achieved objective***

The results of the research carried out in this stage of the project have been presented at international scientific events in the form of oral presentations (**4**), one of them awarded at international conferenceone, and one poster.

***Oral presentations at international scientific conferences:***

1. Mirela-Fernanda Zaltariov**,** NicoletaVornicu, Maria Cazacu, Angelica Vlad, **Evaluation of biological activity of some metal complexes based on flexible Schiff base ligands**, *Apollonia University Days “Preparing the future by promoting excellence*” 3-5 March **2016**, Iasi**– oral presentation**.
2. Mirela Zaltariov**,** Maria Cazacu, Angelica Vlad, Sergiu Shova, **Coordination polymers of bis(p-carboxyphenyl)diphenylsilane and Zinc(II) ions: structural diversity and photoluminescence properties***, SCTE 2016 - 20th International Conference on Solid Compounds of Transition Elements*, April 11th – 15th, Zaragoza, Spania,**2016– *Prize awarded for the oral presentation*.**
3. Angelica Vlad, Mirela Zaltariov, Maria Cazacu, Sergiu Shova, **Synthesis, structure and magnetic properties of manganese-organic frameworks of a V-shaped bis(p-carboxyphenyl)diphenylsilane,***SCTE 2016 - 20th International Conference on Solid Compounds of Transition Elements*, April 11th – 15th, Zaragoza, Spania, **2016 –prezentareorala**.
4. Mirela-Fernanda Zaltariov, Maria Cazacu, GhenadieNovitchi, Cyrille Train, SergiuShova, Vladimir Arion, **Synthesis, structural characterization and ferromagnetic interactions in a silicon-containing chloride-bridged cluster [Co2Cl2(HL)4][CoCl4]·4CH3CN,***ACS on Campus*, University Politehnica of Bucharest*,* May 13, **2016 – prezentareorala.**
5. Mirela-Fernanda Zaltariov, Maria Cazacu, Angelica Vlad, **MOFs built on tri-, tetra-, penta- and infinite nuclear clusters and silane polycarboxylic acids**, *Eighth Cristofor I. Simionescu Symposium Frontiers in Macromolecular and Supramolecular Science, June, 1-2, Iasi,***2016 – poster.**

**🗹*At least two scientific articles submitted at ISI journals***-***achieved objective.***

The results obtained in this stage of the project have been published in ISI journals, their number being larger than expected, **7 published articles, their total impact factor being 15.536.**

**Published articles:**

1. Mirela-Fernanda Zaltariov, Maria Cazacu, Liviu Sacarescu, Angelica Vlad, Ghenadie Novitchi, Cyrille Train, Sergiu Shova, Vladimir B. Arion, *Oxime-Bridged Mn6 Clusters Inserted in One-Dimensional Coordination Polymer*, **Macromolecules**, DOI: 10.1021/acs.macromol.6b01149, **2016**(**F.I. 5.554**).
2. Mirela-Fernanda Zaltariov, Corneliu Cojocaru, Sergiu Shova, Liviu Sacarescu, Maria Cazacu, *Synthesis, structural characterization and quantum chemical studies of silicon-containing benzoic acid derivatives*, **Journal of Molecular Structure**, **2016**, 1120, 302-316 (**F.I. 1.780**).
3. Angelica Vlad, Mirela-Fernanda Zaltariov, Sergiu Shova, Maria Cazacu, Mihaela Avadanei, Alina Soroceanu, Petrisor Samoila, *New Zn(II) and Cu(II) complexes with in situ generated N2O2siloxane Schiff base ligands*, **Polyhedron, 2016**, 115, 76-85 (**F.I. 2.108**).

## [Angelica Vlad](http://pubs.rsc.org/en/results?searchtext=Author%3AAngelica%20Vlad),  [Mirela-Fernanda Zaltariov](http://pubs.rsc.org/en/results?searchtext=Author%3AMirela-Fernanda%20Zaltariov),  [SergiuShova](http://pubs.rsc.org/en/results?searchtext=Author%3ASergiu%20Shova),   [Ghenadie Novitchi](http://pubs.rsc.org/en/results?searchtext=Author%3AGhenadie%20Novitchi),  [Cyrille Train](http://pubs.rsc.org/en/results?searchtext=Author%3ACyrille%20Train),  [Maria Cazacu](http://pubs.rsc.org/en/results?searchtext=Author%3AMaria%20Cazacu), *Metal–organic frameworks based on tri- and penta-nuclear manganese(II) secondary building units self-assembled by a V-shaped silicon-containing dicarboxylate*, RSC Advances, 2016, 6, 37412-37423 (F.I. 3.289).

1. Ana-Maria-Corina Dumitriu, Mihaela Balan, Alexandra Bargan, Sergiu Shova,Cristian-Dragos Varganici, Maria Cazacu, *Synthesis of functionalized silica nanostructure: Unexpected conversion of cyanopropyl group in chloropropyl one during HCl-catalysed hydrolysis of the corresponding triethoxysilane*, **Journal of Molecular Structure**, **2016**, 1110, 150-155 (**F.I. 1.780**).
2. R. I. Gurtovyi, L. V. Tsymbal, S. Shova, Ya. D. Lampeka, *Effect of the structure of aromatic nitro compounds on the efficiency of luminescence quenching of the metal–organic framework of zinc(II) 4,4-diphenyldicarboxylate*, **Theoretical and Experimental Chemistry, 2016,** 52, 44-50 (**F.I. 0.815**).
3. Ana–Maria-Corina Dumitriu, Alexandra Bargan, Mihaela Balan, Cristian-Dragos Varganici, Sergiu Shova, Maria Cazacu, Synthesis and characterization of octakis(3-chloroammoniumpropyl)octasilsesquioxane***,* Revue Roumaine de Chimie** **2016**, 61(4-5), 387-395 **(F.I. 0.21).**

**🗹Scientific report-*achieved objective.***

***Table including some of the synthesized compounds in this stage of the project***

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| **No.** | **Compound/structure type** | **Confirmation and investigation methods** | ***Remarks*** |
| **Objective 1. Preparation of the extended networks based on pre-formed or *in situ* formed metal clusters and the obtained ligands; Expected indicator: at least a novel network containing metallic clusters and flexible bridges; *Achieved objective***  ***1.1.Preparation of the extended networks based on flexible ligands and different metallic precursors – achieved objective.***  ***1.2.Determining the chemical and structural composition of the obtained metal complexes by using physical methods of analysis: elemental analysis, TGA, FTIR (MIR/FIR), EDXRF, XRD - achieved objective.***  ***1.3.Selection of the interest structures and their investigation by SEM, TEM, AFM to evaluate the morphology and porosity; study of the surface properties by DVS - achieved objective.*** | | | |
| **1.** | * ***Preparation of the coordination networks based on the pre-formed tetranuclear cluster[Cu4(μ4-O)(L)2(CH3COO)2]***   **D:\My Documents\Desktop\SCHEMA POLIMERI ACP_CU4.tif**  Synthetic pathway for obtaining the coordination networks P1-P4 starting from the pre-formed cluster [Cu4(μ4-O)(L)2(CH3COO)2].  **D:\RAPORT STIINTIFIC IDEI 2013_MIRELA\2016\shI_3132_MZ.jpg**  XRD structure and FTIR spectrum of the pre-formed tetranuclear cluster [Cu4(μ4-O)(L)2(CH3COO)2].  FTIR spectra of the coordination networks **P1** and **P3**  D:\RAPORT STIINTIFIC IDEI 2013_MIRELA\2016\shI_3104_MC.jpg  XRD structure of network P4 | FTIR (MIR/FIR)  EDXRF  XRD | Indicator of achievement |
| **2.** | Synthetic path for obtaining the coordination network **Zn\_MOF\_1**    FTIR spectra: MIR si FIR of the coordination network **Zn\_MOF\_1**  D:\My Documents\Desktop\p2_.tif  EDXRF spectrum and XRD structure of the zinc oxide clusters in the structure of **Zn\_MOF\_1**  D:\My Documents\Desktop\469_4.tif  XRD structure of the coordination network **Zn\_MOF\_1**  D:\My Documents\Desktop\tg mof 10 mkg.tifD:\My Documents\Desktop\dsc mof 10 mkg.tif  TG/DTG and DSC curves of the coordination network **Zn\_MOF\_1**  D:\My Documents\Desktop\dvs mof a0 mkg.tif  Sorption/desorption isotherms of the water vapors and N2of the coordination network **Zn\_MOF\_1** | FTIR (MIR/FIR)  Elemental analysis  XRD  TG/DTG  DSC  DVS  Sorption of N2 | Indicator of achievement |
| **3.** | Synthetic pathway for obtaining the coordination network **Zn\_MOF\_2**    FTIR and EDXRF spectra of the coordination network **Zn\_MOF\_2**  D:\My Documents\Desktop\P1_3cps.tif**D:\My Documents\Desktop\dvs 3cps zn.tif**  3D XRD structure of **Zn\_MOF\_2** and sorption/desorption isotherms of water vapors  **D:\My Documents\Desktop\tg 3cps.tifD:\My Documents\Desktop\dsc 3cps zn.tif**TG/DTG and DSC curves of Z**n\_MOF\_2** | FTIR (MIR/FIR)  Elemental analysis  XRD  TG/DTG  DVS | Indicator of achievement |
| 4. | XRD structure of the coordination polymer [MnIII6(µ3-O)2(salox)6(H2salox)(μ-L)(H2O)3]n    Size distribution of the aggregates formed in DMF (a) and chloroform (b).  D:\DRAFTURI\LUCRARE MN6\Mn 6 aprilie 2016\figuri Mn6\f9.tif  TEM images of the aggregates obtained from DMF (a), chloroform (b), by evaporation of the solvent; SEM images of the film from chloroform (c), the structural representation of a vesicle (d).    AFM images of the film formed by evaporation of the solvent in the absence of magnetic field (left) and in the presence of the magnetic field (right) at room temperature and pressure | Evaluation of morphology by SEM, TEM, AFM și DLS | Indicator of achievement |
| **Objective 2. Evaluation of some properties and potential applications for the obtained metallo-silicon networks; Expected indicator: The results of at least an applicability test for three networks; *Achieved objective***  2.1. Testing of the networks in hosting various guest molecules acting as storage, separation, catalysis, etc.- ***Achieved objective*** | | | |
| **1.** | * ***Evaluation of antimicrobial properties of some Cu2+and Zn2+complexes with Schiff base ligands*** | The studies have been carried out on three species of fungi (Aspergillusfumigatus ATCC 66567, Penicilliumchrysogenum ATCC 20044, Fusarium ATCC 20327 ) and two species of bacteria(Pseudomonas sp. ATCC 15780 și Bacillus sp. ATCC 31073) | Indicator of achievement |
| **2.** | * ***Evaluation of emission (fluorescence) properties of some metal complexes and extended networks based on Zn2+and Sciff base and carboxylic acid ligands***       Fluorescence spectra of a-[Zn(LA)2] şi b-[Zn(HLB)2(H2O)2]2+ | UV-vis  Fluorescence | Indicator of achievement |
| **3.** | * ***Evaluation of catalytic properties in hydrocarboxylation of linear and cyclic alkanes of the complex [Cu4(μ4-O)(L2)2Cl4]***     Hydrocarboxylation in one step in mild conditions of alkanes C*n* (*n* = 5−8) in carboxylic acids C*n*+1in the presence of the catalyst[Cu4(μ4)(L2)2Cl4]  Versatility of the substrate and selectivity in the direct hydrocarboxylation of the linear and cyclic alkanes in the presence of the copper catalyst     * ***Peroxidative oxidation of cyclohexane***   Oxidation of cyclohexane to cyclohexanol and cyclohexanone in the presence of the copper catalyst [Cu4(μ4)(L2)2Cl4] | Hydrocarboxylation of linear and cyclic alkanes;  Peroxidative oxidation of cyclohexane;  Oxidation of 1-phenylethanol by microwaves irradiation in the absence of the solvents; | Indicator of achievement |
|  | Total yield (cyclohexane and cyclohexanone) depending on time in oxidation of cyclohexane by H2O2 (50% aqueous solution) at 50 °C in CH3CN in the presence of copper catalyst     * ***Oxidation of 1-phenylethanol by Microwave-irradiation in absence of solvents***     Oxidation of 1-phenylethanol to acetophenone by microwave irradiaon, in absence of solvents, in the presence of the catalyst[Cu4(μ4)(L2)2Cl4]  The results of catalysis in the presence of copper complex of the oxidation of 1-phenylethanol to acetophenone by microwave irradiation |  | Indicator of achievement |
| **4.** | ***Testing of the networks in hosting various guest molecules acting as storage, separation, catalysis***   * ***Evaluation of gas sorption (H2and N2)***   Sorption data for the coordination network [Zn2(azopy)2H2L]n      Sorption/desorption isotherms of H2and N2and XRD structure of the network [Zn2(azopy)2H2L]n    XRD structure and sorption/desorption isotherms of N2of the coordination network *{[Zn2(COO)4(DMF)2]·0.8DMF}n*   * ***Estimated accessible volume for different guest molecules: water vapors, N2, H2, CO2of the coordination networksZn\_MOF\_1 and Zn\_MOF\_2*** | Gas sorption  DVS  Olex2  Mercury software | Indicator of achievement |
|  | Theoretical estimated free accessible volume at different guest molecules of Zn\_MOF\_1    Theoretical estimated free accessible volume at different guest molecules of Zn\_MOF\_2 |  |  |

***All the objectives of this project stage, 2016, were met as planned achievement!***