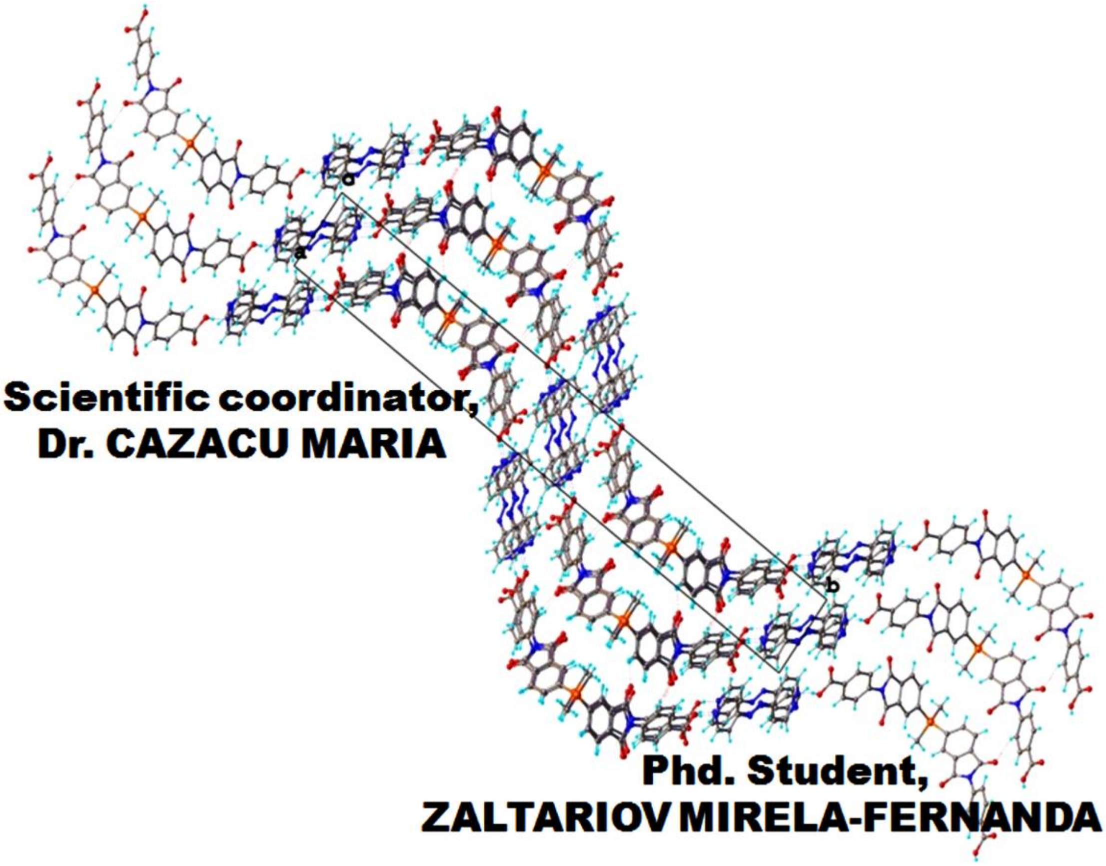
ROMANIAN ACADEMY

"PETRU PONI" INSTITUTE OF MACROMOLECULAR CHEMISTRY IAŞI

Dedicated to the 65th anniversary of "Petru Poni" Institute of Macromolecular Chemistry of Romanian Academy, Iași, Romania

METAL COMPLEXES, COORDINATION POLYMERS AND NETWORKS BASED ON SILOXANE AND SILANE LIGANDS

-Abstract-



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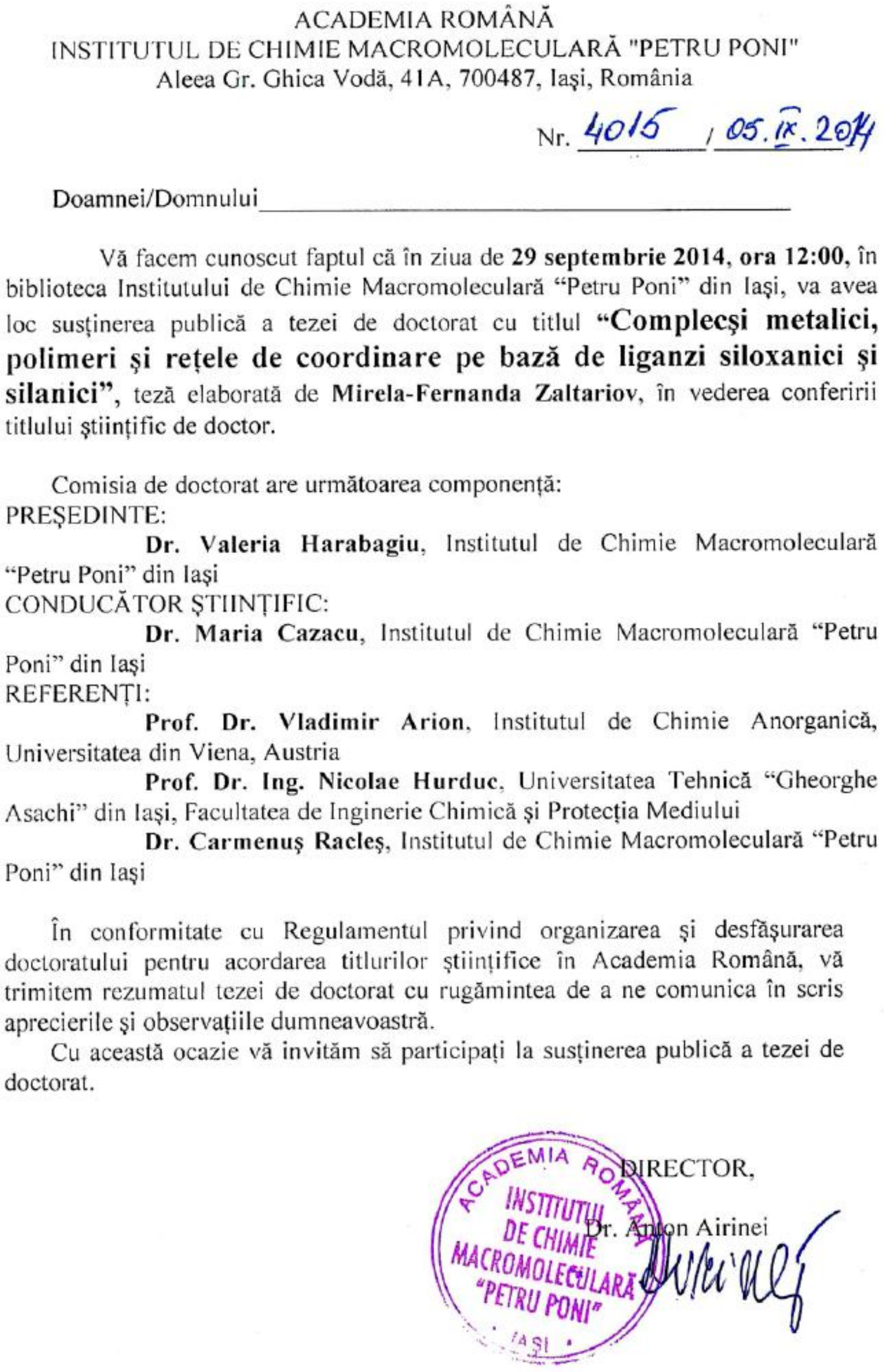

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Nr. 4015 / 05.IX.2014

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Vă facem cunoscut faptul că în ziua de **29 septembrie 2014, ora 12:00**, în biblioteca Institutului de Chimie Macromoleculară "Petru Poni" din Iaşi, va avea loc susţinerea publică a tezei de doctorat cu titlul **"Complecşi metalici, polimeri şi reţele de coordinare pe bază de liganzi siloxanici şi silanici"**, teză elaborată de **Mirela-Fernanda Zaltariov**, în vederea conferirii titlului ştiinţific de doctor.

Comisia de doctorat are următoarea componenţă:

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În conformitate cu Regulamentul privind organizarea şi desfăşurarea doctoratului pentru acordarea titlurilor ştiinţifice în Academia Română, vă trimitem rezumatul tezei de doctorat cu rugămintea de a ne comunica în scris aprecierile şi observaţiile dumneavoastră.

Cu această ocazie vă invităm să participaţi la susţinerea publică a tezei de doctorat.

DIRECTOR,

Dr. Anton Airinei

Thanks

Special thanks and gratitude to the scientific coordinator, ***dr. Maria Cazacu****, for trust, professionalism and competent scientific guidance throughout the period of research and elaboration of the thesis, for useful recommendations and continuously support given in my formation as a researcher.*

Thanks, respect and gratitude to ***Mr. Acad. Constantin Turtă*** *for initiation in the field of coordination chemistry, for continuous advice and encouragement offered during the doctoral internship.*

My whole consideration and gratitude to ***Prof. Dr. Sergiu Shova****, for his help in the characterization of the compounds by single-crystal X-ray diffraction, for useful advice and support provided in the synthesis and characterization of metal complexes during the doctoral internship.*

Grateful thoughts to ***dr. Valeria Harabagiu****, and to* ***dr. Carmen Racleş****,* ***Prof. Dr. Arion Vladimir*** *and* ***Prof. Dr. Nicolae Hurduc*** *who have honored me, as president and referees, respectively, in the PhD committee, for their patience in analyzing the thesis, as well as for the suggestions made.*

Thanks and gratitude to ***Ms. Angelica Vlad*** *and* ***Mr. Haulica Valerică*** *for help, encouragement and useful advice provided during doctoral internship and to laboratory colleagues:* ***Mihaela Alexandru, Alexandra Bargan, George Ştiubianu, Alina Soroceanu, Ana-Maria-Corina Dumitriu, Mihai Iacob, Adrian Bele, Codrin Ţugui*** *and* **Ioan Macsim** *for their support during the realization of this work.*

Thanks to **all my colleagues** *from* **"Inorganic Polymers" Department** *and from* ***"Petru Poni" Institute of Macromolecular Chemistry*** *for their support in characterization of the compounds presented in the thesis***.**

Thanks to Romanian Academy for the financial support during the training period of the PhD. thesis (2010-2014).

In particular I would like to thank **my family***, especially to my son,* **Nectarie***, and to my husband,* **Iulian,** *for their moral support, trust and constant encouragement, dedicating them this success.*

Thanks and gratitude to **Gruia and Cristina Jacotă family** *for permanent and unconditionally support offered.*

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Keywords: siloxane and silane ligands, flexibility, supramolecular structures, self-assembly, coordination polymer, single crystal X-ray diffraction, catalysis.

List of abbreviation

MOFs	Metal-organic frameworks	**T_g (^oC)**	Glass transition temperature
FTIR	Fourier transform infrared spectroscopy	**T_{cr} (^oC)**	Crystallization temperature
^{1}H NMR	Proton nuclear magnetic resonance	**T_m (^oC)**	Melting temperature
^{13}C NMR	Carbon nuclear magnetic resonance	**N2O2**	Coordination by two nitrogen atoms and two oxygen atoms
TG	Thermogravimetrical analysis	**NO2**	Coordination by one nitrogen atom and two oxygen atoms
DTG	Differential thermogravimetrical analysis	**NO**	Coordination by one nitrogen atom and one oxygen atom
DSC	Differential scanning calorimetry	**N2O**	Coordination by two nitrogen atoms and two oxygen atoms
SBUs	Secondary building units	**W_m (%)**	The mass loss rate corresponding to T_{max} values
1D	One-dimensional	**W_{rez} (%)**	The percent of residue remaining at the end of thermal degradation
2D	Two-dimensional	**PAZ**	Polyazomethine 1
3D	Three-dimensional	**PAZ2**	Polyazomethine 2
DVS	Dynamic water vapour sorption	**THF**	Tetrahydrofuran
XRD	Single crystal X-ray diffraction	**K_s**	Stability constant
DMF	N,N'-dimethylformamide	**DMSO**	Dimethylsulfoxide
XRF	X-ray fluorescence spectrometry	**Eg**	Gap energy
$CDCl_3$	Deuterate chlororfom	**$\Delta\nu^a$**	Stokes shift
CH_2Cl_2 sau DCM	Dichloromethane	**TFA**	Trifluoracetic acid
MS	Mass spectrometry	***ε****	Complex dielectric permittivity
CM	Molar concentration	***ε'***	Dielectric constant
λ_{abs}	Maximum of absorption	***ε''***	Dielectric loss
λ_{em}	Maximum of emission	**SP1**	Supramolecular polymer 1
λ_{exc}	Excitation wavelength	**SP2**	Supramolecular polymer 2
MeOH	Methanol	**SP3**	Supramolecular polymer 3
ACN	Acetonitrile	**MIC**	Minimum inhibitory concentration
CCDC	Cambridge Crystallographic Data Centre	**tmds**	Tetramethyldisiloxane
T_{on}	Onset thermal degradation temperature	**imH sau HIm**	Imidazole
$T_{max.}$	Maximum temperature of the decomposition process	**azopy**	Azopyridine
T_{of}	End-temperature of the decomposition process	**salox**	Salicylaldoxime
$\chi_M T$	Magnetic susceptibility	**GPC**	Gel permeation chromatography
AFM	Atomic force microscopy	**Sci**	Core fluid retention index
Sa (nm)	Average roughness	**Sdr(%)**	Developed interfacial area ratio
Sq (nm)	Root mean square roughness	**Stdi**	Texture direction index
		hcpdps	bis(*p*-carboxyphenyl)diphenylsilane acid

INTRODUCTION

The rapid development of the metal-organic chemistry in the early 1950s, resulted in the emergence of a variety of remarkable and molecular structures and of the new compounds involved in catalysis, nonlinear optics, electronics, photoluminescence, adsorption, separation and gas storage, etc.

Coordinative chemistry provides the means for the design of such structures, as the metal ions and ligands relates naturally and spontaneously with each other via the coordinative interactions, giving rise to a variety of structures, from discrete to the extended architectures.

Depending on the chemical structure of the ligands, metal-organic frameworks can be rigid or flexible and dynamic by exposure to certain stimuli. The structural flexibility is a unique and interesting property for selective adsorption and separation, but difficult to achieve with rigid porous structures.

The design of such structures with specific functionalities and properties represents a permanent aspiration for scientists. The combination of those two components of MOFs: metal ion, or cluster and organic ligand, offers infinite possibilities.

Carboxylic ligands, such as aromatic ones, especially di- and tricarboxylic acids, proved to be a convenient alternative to obtain metal-organic frameworks that exhibit a remarkably high surface, with uniform distribution of pore sizes. Their main disadvantage is their lack of stability in the air and in the presence of moisture, which is a significant issue in the case in which it would be used in industrial or commercial applications. To this aim, a number of researchers have investigated different methods to improve stability in the presence of humidity, through the incorporation of methyl groups close to the coordination sites or by postsynthetic strategy incorporation of the hydrophobic groups.

In this context, our efforts have been directed towards the development of strategies for obtaining metal-organic frameworks based on siloxane or silane ligands which will provide both flexibility (through the siloxane bond) and hydrophobicity (due to dimethylsilane or dimethylsiloxane sequences).

Taking into account the characteristics of the building blocks of the proposed structures (nonpolar and flexible silicone component versus the rigid and polar complexed metal), theme addressed in this thesis is of a great difficulty in terms of synthesis and characterization, but constitutes a big challenge due to very interesting properties that can develop these compounds: amphiphilic character, stimuli response, adaptability, etc.

The doctoral thesis entitled "METAL COMPLEXES, POLYMERS AND COORDINATION NETWORKS BASED ON SILOXANE AND SILANE LIGANDS" has as general objective the synthesis and characterization of new metal-organic compounds, from discrete molecules to extensive networks having in the structure siloxane or silane units, with applications in catalysis, gas storage, biology (as antimicrobial agents), luminescent devices, etc.

To achieve the general objective, following specific objectives were carried out:

- ✓ Synthesis of new amine and carbonyl compounds having siloxane or silane units in the structure;
- ✓ Obtaining appropriate ligands with siloxane or silane sequences: Schiff bases and carboxylic acids;
- ✓ Preparation of metal complexes starting from *3d* metal ions and ligands containing siloxane or silane units;
- ✓ Preparation of polymers having pendant complexing groups and their use in coordination of *3d* metal ions;
- ✓ Synthesis of polymers and supramolecular structures based on siloxane and silane ligands and metal ions (*3d*);
- ✓ Evaluation through specific techniques of the properties and potential applications of the ligands, metal complexes and coordination networks.

INTRODUCTION

The thesis consists of two parts, being divided into seven chapters. The paper expands on 369 pages and contains 279 figures, 35 schemes, 51 tables and 470 references.

The first part presents a summary of the literature data on the development of coordination compounds. The second part is structured into six chapters and presents the original contributions in the field of metal-organic compounds which have in the structure siloxane or silane units.

Chapter I is a literature study on the present state of the research in the field of metal complexes and provides details on the design principles of metal-organic porous structures and posibilities for their characterisation through specific methods: X-ray diffraction for structural confirmation, gas sorption in order to assess them in terms of porosity and gas storage capacity. The strategies in obtaining coordination networks are presented in order to achieve an easy guided process of structural synthesis, by choosing suitable ligands (rigid or flexible) and connectors (metal ions or clusters), and strategies for the optimization of voids in order to increase the capacity and selectivity for gas storage and separation of active principles.

Chapters II, III, IV, V and **VI** describe original contributions for synthesis, structural characterization by single crystal X-ray diffraction, evaluation of the properties and application areas of the new metal complexes with discrete and extended structure on the basis of new ligands with siloxane or silane segments.

Chapter II describes the methods of obtaining and characterisation of new amines and aldehydes, derived Schiff bases and carboxylic acids containing siloxane sequences or silane units within structure.

Chapter III presents the results obtained by the complexation of the synthesized ligands with *3d* metal ions (Cu^{2+}, Zn^{2+} and Co^{2+}). By varying the conditions of synthesis and crystallization, metal complexes with discrete or extended structures and different coordination geometries were obtained.

Chapter IV describes synthesis and characterization of the coordination polymers based on macromolecular ligands with pendant~~e~~ complexing groups and *3d* metals (Cu^{2+}, Co^{2+}, Zn^{2+}) having in the structure siloxane sequences or silane units.

Chapter V describes the original results regarding coordination polymers and supramolecular structures of the ligands containing siloxane and silane segments and *3d* metals using self-assembly strategy and is structured into five subchapters. The first subchapter, V.1., presents the synthesis and characterization of supramolecular polymers of the ligands having silane units in their structure by intermolecular noncovalent interactions: hydrogen bonds and π-π stacking interactions. Subchapters V.2-V.5 describe the synthesis of coordination polymers and metal-organic networks-based on siloxane or silane ligands and *3d* metal ions, and are structured according to the coordinated ions. Subchapter V. 2. presents the obtained 1D and 3D metal-organic frameworks containing Cu(II). In subchapter V.3., various methods are described (solvothermal or nonsolvothermal) for the preparation of metal-organic networks based on secondary building units (SBUs) - polynuclear clusters of manganese - and various dicarboxylic acids as structural 1 D, 2D and 3D extension. Another subchapter, V.4., is devoted to obtaining and characterization of new metal-organic networks based on ligands with siloxane and silane units in the structure and Zn(II) ions, in presence or absence of co-ligands. The last subchapter, V.5., presents results related to 1 D and 2D coordination networks based on carboxylic ligands with siloxane sequence in the structure and Co(II) ions, in the presence of 4,4'-azopyridine and salicylaldoxime as co-ligands.

Chapter VI presents the results of tests evaluating the potential applications of the ligands with siloxane and silane sequences as well as of the metallic complexes derived from them in the field of biology as antimicrobial agents. For a part of the synthesized ligands, metal complexes and metal-organic networks with Zn(II) ions in the structure, photoluminescence properties were evaluated. There are also described the results of the catalytic activity evaluation of a tetranuclear complex of Cu(II) in hydrocarboxylation of linear and cyclic alkanes, in peroxidative oxidation of cyclohexane and solvent-free microwave-assisted oxidation of 1-phenylethanol. For a Co(II) complex was tested the efficiency of its use as a filler in silicone matrix, in order to increase the dielectric constant, of interest to the engineering of artificial muscles.

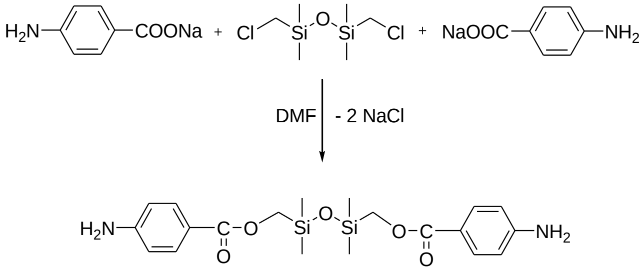
Chapter VII is the experimental section of the thesis and presents the materials used in the synthesis of the compounds, characterization methods and crystallization techniques.

The thesis ends with the presentation of the General conclusions and bibliography.

The abstract of the thesis presents several results described in chapters II, III and V, the final conclusions, bibliography and the dissemination of the scientific results. Numbering of chapters, tables and schemes as well as the references are the same with those presented in the thesis.

Original contributions

Starting from the premise that the Si-O-Si large and flexible angle ranging between 135^o and 180^o might confer some special features, our objective was to obtain new N2O2 ligands with siloxane sequence in the structure using a new siloxane diamine (Scheme 1) (Chapter 1.1.) (153).



1

Schema 1. Synthesis pathway leading to siloxane diamine, *1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(methylene)-bis(4-aminobenzoate),* ***1***

Single crystal X-ray diffraction of the diamine ***1*** reveals a molecular structure composed from neutral entities (**Figure 15**). The main crystal structure motif can be characterized as 2D layers formed via a system of N1-H ...O1 hydrogen bonds (**figures 16 and 17**) (Chapter 1.2).

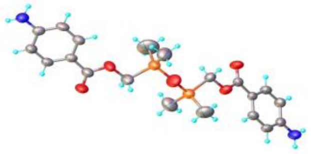


Figure 15. Molecular structure of diamine **1**

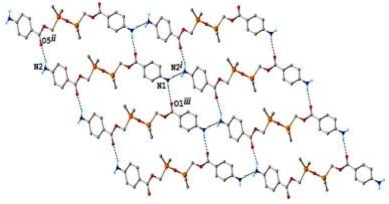


Figure 16. The association of the molecules 1 through N–H· · ·O hydrogen bonds in the crystal

Figure 17. The view of two-dimensional supramolecular double layer in the crystal structure 1

Schiff bases were obtained by condensation of the siloxane diamine with different carbonylic compounds (Chapter 1.3). Structural studies have revealed that the molecules are in *cis* conformation, the aromatic rings being oriented on the same side with respect to siloxane moiety. This is attributed specially to the flexible Si-O-Si angle, and it can be seen in different values of Si-O-Si angle and Si-O distances depending on the nature of the substituent on the aromatic ring (table 4) (Chapter 1.4.).

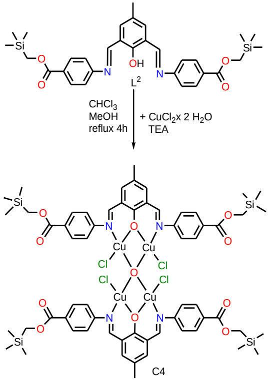
Table 4. Si-O-Si bond angles and bond distances for compounds **2-5**

Parameter	**1**	**2**	**3**		**4**		**5**
			A	B	A	B	
Si-O Length	1.614(2); 1.608(2)	1.624(2); 1.637(2)	1.623(3); 1.628(3)	1.625(3); 1.638(3)	1.577(3); 1.600(3)	1.603(3); 1.526(3)	1.629(1)
Si-O-Si Angle	158.1(2)	147.4(1)	146.5(2)	143.9(2)	158.9(2)	172.0(3)	153.8(3)

Structural diversity of metal complexes with Schiff bases ligands and the evaluation of the properties-structure relations have been extensively studied in recent years (186-190).

Concerns in the field of metal complexes with Schiff bases ligands are one of the objectives of this thesis and confirm an intensive research in the area of coordination compounds with siloxane sequence in the structure (127,128, 131-133, 203-205), by description of new metal complexes derived from Schiff bases ligands with trimethylsilyl units, as discrete or extended structures (Chapter III.1.).

Thus, by complexing of the ligand 12 (L2) with Cu(II) ions (**scheme 14**), a tetranuclear complex was obtained, whose structure was established by single crystal X-ray diffraction (**figure 130**) (Chapter III.3.). Copper complex crystallizes in the space group *Pbca*, without any solvent molecule co-crystallized. The central part of the complex consists of a tetranuclear {Cu_4} core held together by a μ_4-oxido ligands. Two mono-deprotonated ligands (**L_2**) are coordinated to the four copper (II) ions through four nitrogen atoms and two phenolato oxygen donors. The slightly distorted square-planar geometry of each metal ion is completed by a chloride anion and the central μ_4-oxido ligand. The four copper ions are located at the vertices of a distort tetrahedron around the central μ_4-oxido ligand with: ∠Cu1O1Cu2 103.4(4)°, ∠Cu3O1Cu4 103.1(4)°, ∠Cu1O1Cu4 106.8(4)°, ∠Cu2O1Cu3 114.9(5)°. (Chapter III 3.1) (217).



Scheme 14. Synthesis of $[Cu_4(\mu_4\text{-}O)(L^2)_2Cl_4]$, C4

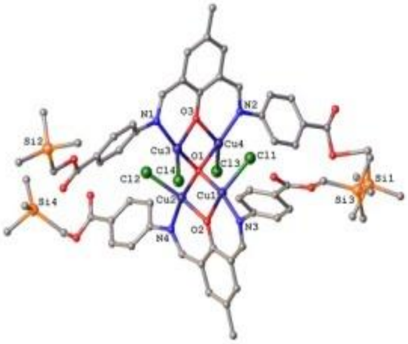


Figure 130. X-ray diffraction structure of $[Cu_4(\mu_4\text{-}O)(L^2)_2Cl_4]$

Carboxylic acids are the most frequently used and studied ligands. Different of those reported in the literature, carboxylic ligands having siloxane sequence in the structure constitute an original approach in the design of metal-organic frameworks with conformational flexibility. By treating 1,3-bis (*p*-carboxyphenylene-ester-methylene)tetramethyldisiloxane acid (Chapter 4.1) (171) with imidazole in the presence of $Cu(OH)_2$, $[Cu(HIm)_4(H_2O)_2]^{2+}$(L^{2-}) complex was obtained, whose structure was confirmed by single crystal X-ray diffraction (Chapter V. 2.2.). The crystal structure of complex comprises $[Cu(HIm)4(H2O)2]^{2+}$ complex cations, L^{2-} anions and statistically distributed solvate water molecules in 1:1:4.5 ratio. A view of the asymmetric part of the unit cell is shown in **figure 201.**

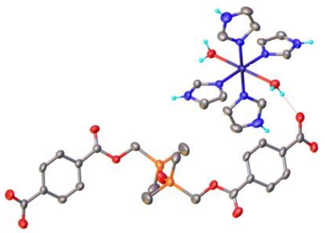


Figure 201. View of the asymmetric part of the unit cell in the crystal structure of $[Cu(HIm)_4(H_2O)_2]^{2+}$(L^{2-})

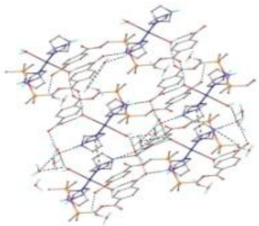


Figure 202. 3D network of $[Cu(HIm)_4(H_2O)_2]^{2+}$(L^{2-})

Double deprotonated tetramethyldisiloxane-containing dicarboxylic acid (L^{2-}) counter-anion is in a fully *transoid* conformation and does not coordinate to copper atom. In the crystal, the discrete $[Cu(HIm)4(H2O)2]^{2+}$ and L^{2-} ions are connected by the coordinated and solvated water molecules into a 3D supramolecular network through intermolecular O-H···O (**figure 202**). In this arrangement, the 3D architecture is consolidated by numerous N-H···O hydrogen bonds formed between coordinated imidazole molecules as donors and oxygen atoms of carboxylate groups and water molecules as acceptors. The supramolecular structure is stabilized by π-π stacking interactions between adjacent centrosymmetrically related imidazole rings, evidenced by the short (3.652 Å) centroid-to-centroid distance (Chapter v. 2.2.2.).

A particularly interesting concept in supramolecular chemistry is the supramolecular polymer, consisting in an array of low molecular weight molecules linked by directional, non-covalent interactions, in order to form linear chains (289). In order to obtain supramolecular polymers with dimethylsilane units, SP1, SP2 and SP3, bis[N-(*p*-carboxyphenyl)phtalimidyl]dimethylsilane acid has been used and three pyridine derivatives: 4,4`-bipyridyl, 1,2-bis(4-pyridyl)ethylene, and 4,4'-azopyridine (**Scheme 21**) (Chapter V.1.3.). Supramolecular polymers resulting from self-assembly of bis[N-(*p*-carboxyphenyl)phtalimidyl]dimethylsilane acid with 4,4`-bipyridyl and 4,4'-azopyridine were obtained in the form of single crystals suitable for X-ray diffraction. The main packing motif is the same in both crystals, and is represented by a wavy chain formed by an alternate sequence of 4,4'-bipyridyl (for **SP1**), 4,4'-azopyridine (for **SP3**) and bis[N(3-carboxyphenyl)phtalimidyl]dimethylsilane molecules linked by O-H···N hydrogen bonds between carboxylic groups as donor and the nitrogen atoms as acceptor. The extension of the crystal structure in both co-crystals occurs through numerous C-H···O contacts, which sustains a 3D two-component supramolecular architecture, shown in **figures 187 and 188** (Chapter V.1.4.). The morphology in film of the supramolecular polymers was studied by AFM revealing a compact, globular morphology in the case of SP1, a bundle, adopting coiled superstructures in the case of SP2 and a structuration characteristic to a porous material in the case of SP3 (313) (**figure 191**) (Chapter V.1.6.).

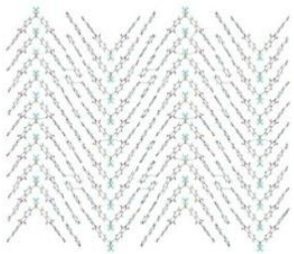
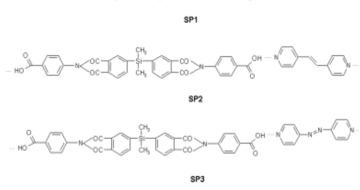


Figure 187. Crystal structure packing in **SP1**



Scheme 21. Chemical structure of the supramolecular polymers, SP1, SP2, and SP3

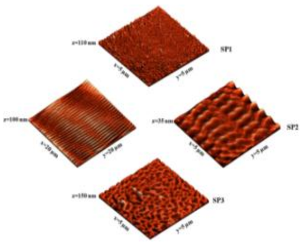


Figure 191. Tapping mode 3D height AFM images of the samples SP1-SP3 prepared on flat surface

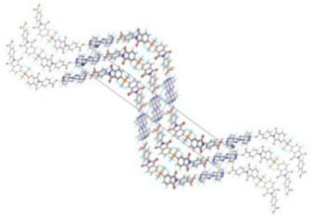


Figure 188. View of the crystal structure along *a* crystalographic axis in **SP3**

Self-assembly of 1,3-bis(carboxypropyl)tetramethyldisiloxane acid with 4,4'-azopyridine through hydrogen bonds results in formation of a 1D supramolecular chain, as can be seen in **Figure 261**. A re-organization of the supramolecular structures occurred by introducing the metal salt, due to the ability of the carboxyl groups and pyridyl fragments to coordinate Co(II) ions (**figure 264**) (Chapter V.5.1).

Single crystal X-ray diffraction analysis indicates the formation of 2D coordination network constructed from CoN2O4 sites linked through 1,3-bis(carboxypropyl)tetramethyldisiloxane and 4,4'-azopyridine spacer as bridging ligands (**figure 265**) (419).

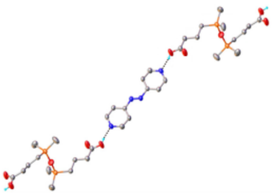


Figure 261. The view of H-bonded 1D chain in crystal structure

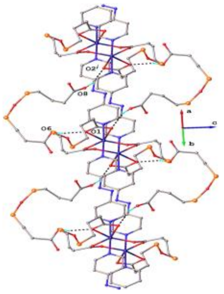


Figure 265. View of 2D layer along [110] crystallographic axis of {[Co(azopy)H$_2$L]H$_2$L}$_n$

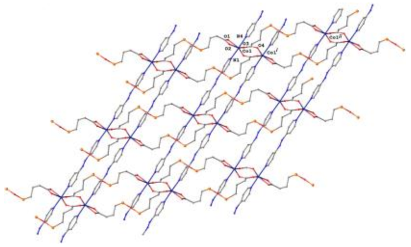


Figure 264. 2D coordination network {[Co(azopy)H$_2$L]H$_2$L}$_n$.
Symmetry codes: i) -x; 1-y; 1-z; ii) -x-1; -y; 1-z.

Special attention in MOFs design was attributed to secondary building units (SBUs) in order to obtain new coordinative compounds with structures and preset dimensionality using carboxylic polydentate ligands (393-395). Considering the various possibilities in the design of such structures, our goal was to obtain polymers and coordination networks based on carboxylic acids with siloxane or silane sequences using polynuclear clusters as SBUs. Thus, starting from bis (*p*-carboxyphenyl)diphenylsilane, in the presence of Mn(II) ions, in DMF, in solvothermal conditions, a 3D structure containing a trinuclear SBU [Mn3] was obtained (**figure 231**). Each Mn atom has a slightly distorted octahedral O_6 coordination. There are four bidentate-bridging (k^1-k^2)-μ carboxylate ligands coordinated to Mn1 atom in equatorial plane. By contrary, Mn2 atom is surrounded by two bidentate-bridging and two monodentate carboxylate ligands (**figure 231**). The coordination of the manganese atom is completed by two μ-H_2O and two DMF molecules as monodentate ligands in apical positions. All monodentate carboxylate ligands are partially protonated and are involved as acceptor in hydrogen bonding with coordinated aqua ligands, which contribute to additional consolidation of [Mn3] cluster. A fragment of 3D network in the crystal structure is shown in **figure 232**. Each trinuclear [Mn3] cluster are interacting with four adjacent [Mn3] units via eight double deprotonated dipolar silicon-centered connectors generating a network topology as can be seen in **figure 232**. The crystal structure packing essentially results from the packing of these 2D networks parallel to 110 plane, as shown in **figure 233** (Chapter V.3.2.1.).

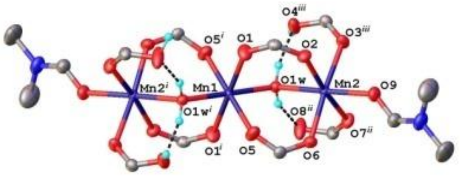


Figure 231. A view of trinuclear [Mn3] cluster in the crystal structure of {$Mn_3(\mu\text{-}H_2O)_2(Hcpdps)_2(cpdps)_2(DMF)_2]\cdot 2DMF\cdot 12H_2O$}$_n$

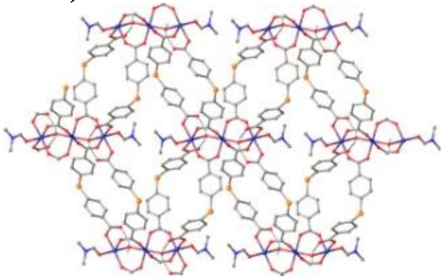


Figure 232. View of 3D network in the crystal structure of {$Mn_3(\mu\text{-}H_2O)_2(Hcpdps)_2(cpdps)_2(DMF)_2]\cdot 2DMF\cdot 12H_2O$}$_n$

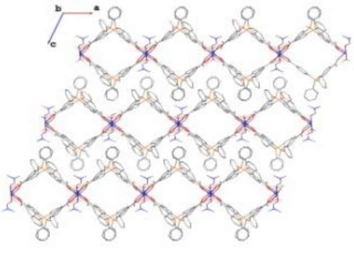


Figure 233. View of the crystal structure along the crystallographic axis *b*

GENERAL CONCLUSIONS

The results obtained and the data presented in this thesis allow formulation of general conclusions:

- ➢ 46 new compounds were synthesized and structurally characterized by spectral methods and single crystal X-ray diffraction (4 amines, 6 acids, 1 aldehyde, 1 anhydride, 1 macrocycle, 11 Schiff bases, 6 polymers and supramolecular structures, 6 metal complexes, 2 1D-coordination polymer, 8 coordination networks 1D-1, 2D-3, 3D-4) containing either siloxane or silane units within the structure. 23 of these compounds were already recorded in the CCDC database. Two macromolecular ligands (polyazomethines) and 6 metal complexes derived from them have been also synthesized and characterized by spectral methods.

●***Schiff bases ligands***

- ✓ New amines and carbonylic derivatives have been prepared and used to obtain the Schiff bases ligands.
- ✓ By condensation of the siloxane and silane-containing diamines with salicylaldehyde derivatives, new Schiff bases different substituted to aromatic ring were obtained. Their structures were confirmed by single crystal X-ray diffraction.
- ✓ Depending on the nature of the substituents at aromatic ring, the packing motifs in crystalline structures are different, noncovalent interactions (H-bonds and π-π stacking interactions) being important factors in these arrangements.
- ✓ Optical behaviour of the Schiff bases in solvents with different polarities is influenced by the nature of the substituents at aromatic ring and by length of the spacer between the chromophore groups. Thus, the Schiff bases containing dimethylsilane groups present fluorescence, the emission intensity being determined by the chemical structure, the nature of the solvents and the substitutes at aromatic ring.
- ✓ Schiff bases with siloxane sequence are flexible, crystallographic data highlighting the changes in siloxane angles and different architectures (2D or 3D) in the crystalline structure in dependence on the nature of substituents.

●***Molecular and polymeric coordination compounds of Schiff bases ligands***

- ✓ Schiff bases were used as ligands to coordinate *3d* metal ions (Cu^{2+}, Co^{2+}, Zn^{2+}). Metal complexes were obtained in form of single crystals, their structures being solved by X-ray diffraction analysis.
- ✓ Crystallographic data indicate discrete mono- and polynuclear structures, or 2D and 3D arhitectures depending on coordination geometry of the metal ions, the presence of co-crystallized solvent molecules or functional groups involved in stabilization of the structure by intermolecular forces: H-bonds and π-π stacking interactions.
- ✓ The dialdehydes containing dimethylsilane units or siloxane sequences were used to prepare macromolecular ligands, polyazomethines, by condensation with 2,5-bis(*p*-aminophenyl)-1,3,4-oxadiazole. The presence of the nitrogen atoms in the imine groups and oxadiazole rings allows the coordination of metal ions by the synthesized ligands.
- ✓ The presence of the siloxane or Si-C bonds confers flexibility, that can induces special feature, such as low glass transition temperature (in 41 - 67.5 ^{o}C) range for the compounds with dimethylsilane units in the structure and (-50.61- (-65.54) ^{o}C range for

the compounds with siloxane sequences in the structure). The structural flexibility of the synthesized compounds confers good solubility in polar aprotic solvents, which allows easier evaluation of properties.

- ✓ The presence of the oxadiazole ring in the structure of polyazomethines confers fluorescence and posibility to coordinate metal ions.
- ✓ The presence of the metal ions in the obtained structures leads to the increased values of dielectric constant and conductivity.
- ✓ Thermal stability of the polyazomethines decreases by complexation with metal ions, probably due to catalytic action of the metal in the decomposition process.

●***Carboxylic acids ligands***

- ✓ Carboxylic ligands with siloxane or silane sequences in the structure were synthesized and structurally characterized by single crystal X-ray diffraction.

●***Supramolecular structures obtained on the basis of dicarboxylic acids***

- ✓ Using self-assembly strategy of the carboxylic acids with pyridine derivatives, supramolecular polymers were obtained by donor - acceptor interactions.
- ✓ The structure of the supramolecular polymers was confirmed by single crystal X-ray diffraction analysis.
- ✓ The association constant by H-bonds between the complementary groups (carboxyl and pyridyl) from the structure of the monomers was determinated by FTIR technique having values between $2.1x10^2$ and $4.27x10^2$ dm^3/mol. These values indicate a relatively low polymerization degree. Their polymeric nature was confirmed by the presence of glass transitions on DSC curves.
- ✓ Supramolecular polymers have proven the ability to organize in film, the AFM images revealing different morphologies in dependence on their structure.
- ✓ The moisture behaviour of the supramolecular polymers was also studied, the results sugesting their hydrophobic nature. This behaviour can be changed under the influence of various factors. The increase in temperature results in a significant increase in sorption capacity, because at high temperatures, the rate of H-bond dissociation intensifies favoring the molecular transport. This also highlights the dynamic nature of such structures.

●***Coordination polymers and networks with 3d metal ions and different arhitectures***

- ✓ Using the self-assembly strategy between carboxylic or supramolecular ligands and *3d* metal ions (Cu^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}), coordination polymers and networks with different arhitectures were obtained in dependence on the coordination geometry of the metal ion and self-assembling via noncovalent interactions: hydrogen bonds and π-π stacking interactions.
- ✓ Starting from different ligands, Schiff bases or carboxylic acids, in the presence of imidazole as co-ligand, three coordination networks having various arhitectures were obtained: *1D-coordination network* $[CuL_2]_n$, formed by self-assembly through non-covalent interactions O-Cu of the monomeric units $[CuL_2]$, which resulted by complexation of a bidentate Schiff base with Cu^{2+} ions, a *3D-supramolecular network* $[Cu(HIm)_4(H_2O)_2]^{2+}L^{2-}$ formed by non-covalent interactions between a cationic complex

$[Cu(HIm)_4(H_2O)_2]^{2+}$ and carboxylate anions, (1,3-bis(*p*-carboxyphenylene-ester-methylene)tetramethyldisiloxane), and a *3D metal-organic framework* $\{[Cu_2(\mu_3\text{-}tmds)_2(imH)_4]\cdot H_2tmds\}_n$, formed by self-assembly through coordinative bonds of dinuclear Cu(II) *paddle-wheel* units with carboxylate ligand (1,3-bis(carboxypropyl)tetramethyldisiloxane).

- ✓ Using manganese clusters and manganese-oximate as SBUs, by clasical and solvothermal methods, three coordination networks were obtained on the basis of carboxylic acids containing siloxane sequence or silane units as bridged ligands: *1D coordination polymer* $\{[Mn_6(\mu_3\text{-}O)_2(salox)_6(H_2salox)(H_2O)_3H_2L]\}_n$, formed by hexanuclear metal-oximate clusters and flexible carboxylate bridges (1,3-bis(carboxypropyl)tetramethyldisiloxane); two *3D-coordination networks*:
  $\{Mn_3(\mu\text{-}H_2O)_2(Hcpdps)_2(cpdps)_2(DMF)_2]\cdot 2DMF\cdot 12H_2O\}_n$,and
  $\{[Mn_5L(cpdps)_4(HCOO)_2(H_2O)_2(DMF)_4]\cdot 6DMF\}_n$ having trinuclear and pentanuclear clusters of bis(*p*-carboxyphenyl)diphenylsilane acid in the structure, which acts as a bridged ligand.
- ✓ The interactions between Mn^{2+} ions were studied by variable-temperature magnetic susceptibility measurements revealing antiferromagnetic interactions between the metal ions in complexes.
- ✓ Supramolecular structures formed by self-assembly of carboxylic acids with pyridine and imidazole derivatives as co-ligands reorganize in the presence of Co^{2+} and Zn^{2+} metal ions leading to 2D-coordination networks: $[Zn(H_2L)(imH)_4]_n$, $[Zn_2(azopy)_2H_2L]_n$ and $\{[Co(azopy)H_2L]H_2L\}_n$.
- ✓ By using a carboxylate ligand and Zn^{2+} ions, in solvothermal conditions, a 1D coordination polymer, $Zn_2(COO)_4(DMF)2]\cdot 0.8DMF\}n$, was obtained consisting in dinuclear $[Zn_2(COO)_4(DMF)_2]$ fragments bridged through bis(*p*-carboxyphenyl)diphenylsilane as double-deprotonated ligand.
- ✓ Thermal stability of the complexes studied by thermogravimetrical analysis have revealed different patterns of decomposition in dependence on structure, the nature of the ligands, co-ligands and metal ions which can catalyse the decomposition process.
- ✓ DSC results indicate in all cases the presence of the glass transition, proving the polymeric nature of the coordination polymers and networks. Due to the flexible siloxane sequences or silane units, the values of glass transition temperatures are lower, being in the range 7-76 ^{o}C.
- ✓ The presence of siloxane and silane units in such of structures confers hydrophobicity, which is supported by low values of water vapours sorption capacity in all the cases.
- ✓ The co-existence of the hydrophobic and flexible siloxane units and metal-coordinated polar blocks confers amphiphilic character and ability to self-assembly in solution, depending on concentration and solvents polarity, as well as the structuration in film, adopting different morphologies.

●*Study of some properties of interest for potential applications*

- ✓ The obtained ligands and metal complexes were tested in terms of their applicability potential in areas such as: biology, catalysis, gas storage, fluorescence, or active fillers in silicone matrix.

GENERAL CONCLUSIONS

- ✓ The results have demonstrated that some Schiff bases ligands and metal complexes have a better antimicrobial activity compared with standards cmpounds: Caspofungin and Kanamycin.
- ✓ Tetranuclear $[Cu_4(\mu_4\text{-}O)(L^2)_2Cl_4]$ complex was tested as catalyst precursor in the hydrocarboxylation of C5–C8 linear (n-pentane, *n*-hexane, *n*-heptane and *n*-octane) and cyclic (cyclopentane, cyclohexane, cycloheptane and cyclooctane) alkanes into C6–C9 carboxylic acids (yields: 12-18 % for linear alkanes, and 24 % in hydrocarboxylation of cyclohexane). Copper complex was also tested as catalyst precursor in the peroxidative oxidation of cyclohexane revealing a total yield of 13.2 % and TON of 122, in the presence of TFA as additive, after 60 minutes. Good results, were obtained in oxidation of 1-phenylethanol in a solvent-free microwave-assisted reaction: total yield of 82% in acetophenone and TON of 826.
- ✓ Gas (H_2 and N_2) sorption/desorption isotherms registered for two coordination networks $[Zn_2(azopy)_2H_2L]_n$ and $\{[Cu_2(\mu_3\text{-}tmds)_2(imH)_4]\cdot H_2tmds\}_n$ have indicated low values of sorption capacity at lower pressures. The absence of saturation allows hypothesis of increasing of this parameter at higher pressures on the basis of the intrinsic structural flexibility.
- ✓ Zn(II) complexes and Zn(II) coordination networks have shown fluorescence thus allowing their use as fluorescent markers in different areas.
- ✓ The metal complexes based on siloxane-containing ligands were found to have good compatibility with silicones and induce an increasing in their dielectric permittivity of interest for electromechanical application of the composites prepared on their basis.

SCIENTIFIC ACTIVITY

The results obtained during the doctoral internship are found in 13 scientific articles published in international ISI journals, 4 oral communications and 16 posters presented at different national and international scientific Conferences in the field of coordination chemistry, polymers and and materials.

1. Solvent effects on the photophysical properties of poly[1,4-dihydroxyanthraquinoneimine-1,3-bis(phenylene-estermethylene)tetramethyldisiloxane]
P. Pascariu Dorneanu, M. Homocianu, I.R. Tigoianu, A. Airinei, **M. Zaltariov**, M. Cazacu, *Spectrochim. Acta Part* A, 134, 218–224. **(2015)-** F.I.=2.129, SRI-0.804

2. Tetranuclear copper(II) complexes with macrocyclic and open-chain disiloxane ligands as catalyst precursors for hydrocarboxylation and oxidation of alkanes and 1-phenylethanol
M.-F. Zaltariov, M. Alexandru, M. Cazacu, S. Shova,G. Novitchi, C. Train, A. Dobrov, M. V. Kirillova, E. C. B. A. Alegria, A. J. L. Pombeiro, V.B. Arion, *Eur. J. Inorg. Chem*, DOI:10.1002/ejic.201402578, **(2014)-** F.I.=2.965, SRI-1.628

3. A silicon-containing polyazomethine and derived metal complexes: synthesis, characterization, and evaluation of the properties
M.-F. Zaltariov, M. Cazacu, S. Shova, C.-D. Varganici, L. Vacareanu,V. Musteata, A. Airinei, *Design. Mon. Polym*., 17, 668–683 , **(2014)-** F.I.=2.21, SRI-0.682

4. A Novel siloxane-containing dicarboxylic acid, 1,3-bis(p-carboxyphenylene-ester-methylene)tetramethyldisiloxane, and its derivatives: ester macrocycle and supramolecular structure with a copper complex
M.F. Zaltariov, A. Vlad, M. Cazacu, S. Shova, M. Balan, C. Racles, *Tetrahedron*, 70(16), 2661-2668 **(2014)**- F.I.=2,817, SRI-1.294

5. A 2D metal–organic framework based on dizinc coordination units bridged through both flexible and rigid ligands
A.Vlad, M. Cazacu, **M.F. Zaltariov**, A. Bargan, S. Shova, C. Turta, *J. Mol. Struct*. 1060, 94-101 **(2014)-**F.I.=1,599, SRI-0.507

6. Metallopolymeric structures containing highly flexible siloxane sequence
A.Vlad, M. Cazacu, **M.F. Zaltariov**, S. Shova, C. Turta, A. Airinei, *Polymer*, 54(1), 43-53 **(2013**)- F.I.=3,766, SRI-2.990

7. Flexible linkers and dinuclear metallic nodes build up an original metal-organic framework
A.Vlad, **M.F. Zaltariov**, S. Shova, G. Novitchi, C.D. Varganici, C. Train, M. Cazacu, *CrystEngComm*,15(26), 5368-5375 (**2013)-**F.I.=3,858, SRI-2.198

8. Electroactive composites based on polydimethylsiloxane and some new metal complexes
M. Cazacu, C. Racles, **M.F. Zaltariov**, A.M.C. Dumitriu, M. Ignat, D. Ovezea, G. Stiubianu, *Smart Mater. Struct*., 22 (10), 104008 (**2013)-** F.I.=2,449, SRI-1.793

9. A new diamine containing disiloxane moiety and some derived Schiff bases: synthesis,

structural characterisation and antimicrobial activity
M. F. Zaltariov, M. Cazacu, N. Vornicu, S. Shova, C. Racles, M. Balan, C. Turta, *Supramol. Chem.*, 25(8), 490-502, (**2013)-** F.I.=2.132, SRI-1.460

10. Hydrogen-bonded supramolecular polymers containing dimethylsilane groups: Synthesis, crystal structure, and characterization
M.F. Zaltariov, M. Cazacu, S. Shova, A. Vlad, I. Stoica, E. Hamciuc, *J. Pol. Sci. A .Chem.*, 50(18), 3775-3787 (**2012)-** F.I.=3,245, SRI-1.957

11. **Zaltariov, M. F.,** Vlad, A., Cazacu, M., Avadanei, M., Vornicu, N., Balan, M., Shova, S., *Silicon-containing bis-azomethines: synthesis, structural characterization, evaluation of the photophysical properties and biological activity, Spectrochim Acta A* – accepted, F.I.=2.129, SRI-0.804**.**

12. **Zaltariov, M. F.,** Cazacu, M., Racles, C., Musteata, V., Vlad, A., Airinei, A., *Metallopolymers based on a polyazomethine ligand containing rigid oxadiazole and flexible tetramethyldisiloxane units, J. Appl. Polym. Sci.* – accepted, F.I.=1.64, SRI=1.037.

13. M. Cazacu, A. Vlad, **M.-F. Zaltariov**, S. Shova, G. Novitchi, C. Train**,**
Di- and tetracarboxylic aromatic acids with silane spacers and their copper complexes: synthesis, structural characterization, and properties evaluation, J. Organomet. Chem. (2014) http://dx.doi.org/10.1016/j.jorganchem.2014.10.006, F.I.=2.302, SRI=1.048.

F.I. (TOTAL)=33.241, SRI (TOTAL)=18.202.

Oral Communications:

1. Nanostructures self-assembled through non-covalent bonding of metal complexes with ligands containing siloxane or silane fragments, Mirela-Fernanda Zaltariov, Maria Cazacu, Angelica Vlad, *The 8th International Conference on Modification, Degradation and Stabilization of Polymers,* 31 August-4 September 2014, Portoroz, Slovenia

2. Synthesis, structural characterization and antimicrobial activity of new siloxane Schiff bases ligands
Mirela-Fernanda Zaltariov, Maria Cazacu, Angelica Vlad, Sergiu Shova, *„Iasi Academic Days", The XXIV-a Symposium-Progress in organic and polymeric chemistry,* MACRO IASI 2013, 3-5 octomber 2013.

3. Cu(II) Complexes based on a new ditopic azomethine ligand containing trimethylsilyl groups
M.F. Zaltariov,S. Shova, M. Cazacu, A.Vlad, *18th Romanian International Conference on Chemistry and Chemical Engineering, RICCCE XVIII*, 4-7 september 2013, Sinaia, Romania

4. Supramolecular structures containing highly flexible siloxane groups

SCIENTIFIC ACTIVITY

> Mirela-Fernanda Zaltariov, Maria Cazacu, Sergiu Shova, Constantin Turta, *Fifth Cristofor I. Simionescu Symposium Frontiers in Macromolecular and Supramolecular Science* June 11-13, 2012, Bucharest, Romania

Posters:

1. Flexible and hydrophobic Zn-based coordination polymer: synthesis, structure, and (H_2, N_2) sorption behaviors evaluation
Angelica Vlad, Maria Cazacu, Sergiu Shova, Constantin Turta, Mirela-Fernanda Zaltariov, „*The International Conference dedicated to the 55th anniversary from the foundation of the Institute of Chemistry of the Academy of Sciences of Moldova*” May 28 - May 30, 2014, Chișinău, Moldova

2. Synthesis, structural characterization, photophysical and antimicrobial properties of new Schiff bases containing dimethylsilane units,
Mirela-Fernanada Zaltariov, Mihaela Avadanei, Nicoleta Vornicu, Maria Cazacu, Sergiu Shova, Angelica Vlad, *„The International Conference dedicated to the 55th anniversary from the foundation of the Institute of Chemistry of the Academy of Sciences of Moldova*” May 28 - May 30, 2014, Chișinău, Moldova

3. $Co_{2.5}L(HL)_3Cl_2][CoCl_4]$ cluster-based on a new azomethine ligand containing trimethylsilyl groups,
Mirela-Fernanda Zaltariov, Sergiu Shova, Maria Cazacu, Angelica Vlad, *”The International Conference dedicated to the 55th anniversary from the foundation of the Institute of Chemistry of the Academy of Sciences of Moldova”* May 28 - May 30, 2014, Chișinău, Moldova

4. Hydrogen-bonded supramolecular structure build on the basis of ferrocenecarboxylic acid and 4,4’-azopyridine,
Angelica Vlad, Maria Cazacu, Sergiu Shova, Mirela-Fernanda Zaltariov, „*The International Conference dedicated to the 55th anniversary from the foundation of the Institute of Chemistry of the Academy of Sciences of Moldova”* May 28 - May 30, 2014, Chișinău, Moldova

5. Photophysical properties of some anthraquinone derivatives
Ionut Radu Tigoianu, Anton Airinei, Mirela Zaltariov, Mihaela Homocianu, Petronela Dorneanu, Nicusor Fifere, Maria Cazacu, *The 14-th International Balkan Workshop on Applied Physics*, 2-4 July 2014, Constanța, Romania

6. Optical properties and self-assembling capacity of metal-containing siloxane polyazomethines,
Mirela Zaltariov, Maria Cazacu, Carmen Racles, Angelica Vlad, Mihaela Avădanei, Gabriela Hitruc, Luiza Gradinaru, George Stiubianu, Anton Airinei,*The 14-th International Balkan Workshop on Applied Physics,* 2-4 July 2014, Constanța, Romania

7. Functional and flexible nanostructured coordination polymers
Angelica Vlad, Maria Cazacu, Mirela-Fernanda Zaltariov, *The 8th International Conference on Modification, Degradation and Stabilization of Polymers*, 31 August-4 September 2014, Portoroz, Slovenia.

SCIENTIFIC ACTIVITY

8. Fluorescence spectra of some antraquinone derivatives
I.R. Tigoianu, P. Pascariu-Dorneanu, M. Zaltariov, A.Airinei, M.Cazacu, *„Iasi Academic Days", The XXIV-a Symposium-Progress in organic and polymeric chemistry,* MACRO IASI 2013, 3-5 octomber 2013.

9. Synthesis and characterization of a new metal-organic framework based on Cu(II) ions and siloxane ligands
A. Vlad, M.Cazacu, S. Şova, M. Zaltariov, *„Iasi Academic Days", The XXIV-a Symposium-Progress in organic and polymeric chemistry,* MACRO IASI 2013, 3-5 octomber 2013.

10. New supromolecular structures containing metals
M.F. Zaltariov, A. Vlad, A. Soroceanu, M. Cazacu, S. Shova, *„Iasi Academic Days", The XXIV-a Symposium-Progress in organic and polymeric chemistry,* MACRO IASI 2013, 3-5 octomber 2013.

11. Fluorescence quenching of some antraquinone derivatives. Sensor Applications
I.R. Tigoianu, A. Airinei, M. Zaltariov, M. Cazacu, V. Ribitsch, C.Gruber, *The 13th International Balkan Workshop on Applied Physics and Materials Science,* 4-6 July 2013, Constanța, Romania

12. Cu (II), Co (II) and Zn (II) complexes of a new polyazomethine containing silane units and oxadiazole rings within the chain
Mirela-Fernanda Zaltariov, Maria Cazacu, Angelica Vlad, George Stiubianu, Anton Airinei,*13th International Balkan Workshop on Applied Physics*, Constanța, Romania, 4-6 July 2013

13. Morphological and surface studies of some new supramolecular polymers containing dimethylsilane groups
Mirela-Fernanda Zaltariov, Alexandra Nistor, Angelica Vlad, George Ştiubianu, Maria Cazacu, *"Alexandru Ioan Cuza" University from Iasi Days –The Conference of Faculty of chemistry, 2012 – Iasi* , 25-27 october

14. Metal complexes of the Schiff bases derived from new silicon-containing amine: Synthesis, structural characterization, properties
Mirela-Fernanda Zaltariov, Maria Cazacu, Sergiu Shova, Constantin Turta, *The XVII-th Conference "Physical Methods in Coordination and Supramolecular Chemistry"* - Chişinău, Republic Moldova - October 24-26, 2012

15. Electroactive composites based on polydimethylsiloxane and some new metal complexes
Maria Cazacu, Carmen Racleş, Mirela Zaltariov, Ana-Maria-Corina Dumitriu, Mircea Ignat, George Știubianu, *Second International Conference on Electromechanically Active Polymer (EAP) transducers and artificial muscles,* Potsdam, Germania, 29 May 2012-30 May 2012

16. New ligands containing siloxane or silicon units
Mirela Zaltariov, Alexandru Ciocârlan, Maria Cazacu, Carmen Racleş, Angelica Vlad, George Ştiubianu, *„Iasi Academic Days", The XXIII-a Symposium-Progress in organic and macromolecular compounds,* MACRO IASI 29 september – 1 october 2011.

SCIENTIFIC ACTIVITY

Projects:

1. **“Synthesis and study of the polymeric metallosiloxanes – new materials for catalysis and nanosciences”, (POLISILMET)**

Project POS CCE: ID 570, Cod SMIS-CSNR:12473
Contract no. 129/2.06.2010;
Project Manager: Dr. Maria Cazacu

2. **“New coordination networks containing polyfunctional flexible bridges”**

PN-II-ID-PCE-2012-4
Contract no: 53/ 02.09.2013
Project Manager: Dr. Maria Cazacu

3. **“Coordinative compounds of the transitional elements based on polydentate flexible ligands as biological active agents and precursors for oxide materials”**

PN-II-CT-RO-MD-2012-1
Bilateral Cooperation Program România-Rep. Moldova
Contract no: 690/16.04.2013
Project Manager: Dr. Maria Cazacu

4. **“Coordinative compounds of 3d metals with Schiff bases ligands having siloxane or silane units”**

Bilateral Cooperation Program România-Austria
Contract no: 749/01.01.2014
Project Manager: Dr. Maria Cazacu

Awards/Distinctions

1. ***Excelence Award*** for the presentation of the scientific work „Synthesis, structural characterization and antimicrobial activity of new siloxane Schiff bases ligands” *„Iasi Academic Days”, The XXIV-a Symposium-Progress in organic and polymeric chemistry*, MACRO IASI 2013, 3-5 octomber 2013.
2. ***Certificate of attendance-STREAM SUMMER SCHOOL,*** 8-13 July 2013
3. ***Certificate Bruker-FT-IR training courses***, *“Sample preparation and Surface Analysis”* (26 october 2011) and *“Rapid Scan/Step Scan, Coupling Techniques”* (27 october 2011), Germania.

Internships abroad:

1-30 June 2014- research internship at the Institute of Inorganic Chemistry, University of Vienna, Austria, in Bilateral Cooperation Program România-Austria, **“Coordinative compounds of 3d metals with Schiff bases ligands having siloxane or silane units”**
17-29 June 2013- research internship at the Institute of Chemistry of Moldavian Sciences Academy in Bilateral Cooperation Program România-Rep. Moldova, **“Coordinative compounds of the transitional elements based on polydentate flexible ligands as biological active agents and precursors for oxide materials”**

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Some of the results presented in this thesis were obtained as a result of activities undertaken within the projects: **"Synthesis and study of the polymeric metallosiloxanes – new materials for catalysis and nanosciences"**, POLISILMET co-financed by European Regional Development Fund, Sectorial Operational Programme "Increase Economic Competitiveness ", Priority Axis 2 (SOP IEC-A2-O2.1.2-2009-2, ID 570, COD SMIS-CSNR: 12473, Contract 129/2010) as exploratory research project, and **"New coordination networks containing polyfunctional flexible bridges"** PN-II-ID-PCE-2012-4, Contract no: 53/ 02.09.2013.