ROMANIAN ACADEMY
„PETRU PONI” INSTITUTE OF MACROMOLECULAR CHEMISTRY- IASI

STRUCTURAL AND MORPHOLOGICAL CHANGES INDUCED BY THE PRESENCE OF SILOXANE BLOCKS IN METAL-ORGANIC COMPLEXES

Ph. D. Thesis Abstract

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Iasi, September 2014

Table of contents

This summary contains the main original results obtained. The numbering of chapters, figures, tables and bibliographical references correspond to that found in the thesis.

Keywords: Cu(II) complexes, Schiff bases, disiloxane unit, alcohols, catalytic oxidation, amphiphilic copper complexes, supramolecular structure.

Introduction

In recent years were seen spectacular developments in coordination chemistry with both theoretical and practical implications, especially on the synthesis and study of new compounds with applications in many areas. Coordination compounds represent the “backbone” of modern inorganic chemistry, bio-inorganic chemistry and the chemical industry, being studied because of their use in fields such as medicine, metallurgy, analytical chemistry, biology, bio-inorganic chemistry. Complexing ligands containing groups –O(H), >C=O and –N(H) occupy a special place in coordination chemistry due to their coordination to metal ions.

Currently getting a new complex combination is no longer a fact in itself, with an emphasis on directed synthesis (rational synthesis) of new complexes with certain properties, or in order to verify certain theoretical assumptions. Due to the increased importance of complexes both in theoretical research and in various fields of industry, appeared the need for multilateral studies on the synthesis process and their fundamental properties.

It is well known crucial role of complexes with catalytic activity in biological processes and in the development of qualitative and quantitative analysis methods. Thus, by judicious selection of the coordinating agent, the metal ions can be separated from solutions in which they are in the form of low soluble substances, which allows the identification and determination of their nature, and on the other hand their precipitation can be prevented.

Research purpose

Obtaining transition metal complexes by using original ligands containing siloxane bond and study the effects induced by its presence on the structure and properties of the obtained complexes.

Objectives of the study

-obtaining Schiff base type N,N,O,O ligands of Schiff base type derivated from 1,3-bis(aminopropyl)tetramethyldisiloxane with various aldehydes and perform their structural characterization;
-synthesis of transition metal complexes with ligands of the type covered by the thesis;
-determining the structure and physical properties of obtained complexes;
-the investigation and identification, using appropriate methods, of structural and morphological features of complexes containing siloxane segments;
-study of properties of interest for potential applications of metal complexes obtained.

Structure of the thesis

PhD thesis entitled “Structural and morphological changes induced by the presence of siloxane blocks in metal-organic compounds” is divided into two main parts and includes eight chapters. *The first part* consists of a literature study on the current state in coordination compounds containing siloxane segments. Also are defined the objectives and main purpose of the research. *The second part* is divided into five chapters and includes original contributions in this area.

Chapters I, II, and III summarize the main points of the literature on coordination compounds, siloxane bond, and the coordination compounds containing siloxane segments. The first chapter deals with some aspects of the overall coordination chemistry and Schiff base type ligands which may be used in the process of complexation. Chapter II presents the features of siloxane bond highlighting properties induced by the presence of siloxane bond in coordination compounds. The third section covers the study of literature on this type of compounds.

Chapter IV presents original results on the synthesis and structural characterization of siloxane ligands obtained through the condensation reaction of salicylaldehyde and a number of its derivatives with 1,3-bis(3-aminopropyl)tetramethyldisiloxane or with α,ω-bis(3-aminopropyl) oligodimethylsiloxanes with different lengths of siloxane segment (0, 1.8 and 2.6 Si-O units).

Chapter V contains original contribution on synthetic strategies and characterization of the coordination compounds of transition metal compounds with Schiff bases containing siloxane segments. The compounds were characterized in terms of structure and properties caused by the presence of the coordinated metal and that of the siloxane segment.

Chapter VI describes the structural and morphological changes induced by the presence of siloxane blocks in some of the coordination compounds obtained and considered as representative.

Chapter VII contains original contributions on potential applications of coordination compounds obtained.

In conclusion thesis, **Chapter VIII** summarizes the main conclusions drawn based on the studies and the results presented in the thesis and selected bibliography.

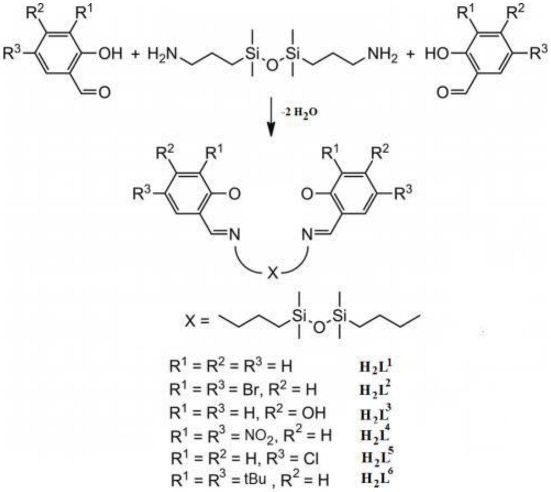
Appendices describe in detail the synthesis and spectral characterization of siloxane and oligosiloxane ligands and coordination compounds, crystallographic data, materials and methods of analysis used, and the list containing the presentations at scientific manifestations and articles published on the scientific results obtained in the doctoral internship.

The results are found in five scientific articles published in international journals, two articles under review, two articles in manuscript, one communication and nine poster presentations at scientific conferences. Some of the activities on which these results were obtained were funded through two research projects in which the author was involved.

The material presented covers 180 pages and contains 82 figures and 25 charts, 32 tables and 323 bibliographic references.

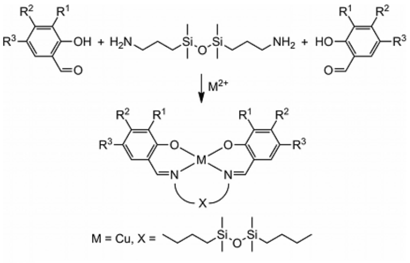
Part II: Original results

The first chapter of the original part of the thesis describes the synthesis and characterization of Schiff base type ligands obtained by condensation reaction of salicylic aldehyde (**H_2L^1**) and some of its derivatives (3,5-dibromo-2-hydroxybenzaldehyde (**H_2L^2**), 2 4-dihydroxybenzaldehyde (**H_2L^3**), 5-nitro-2-hydroxybenzaldehyde (**H_2L^4**), 5-chloro-2-hydroxybenzaldehyde (**H_2L^5**) and 3,5-di-tert-butyl-2-hydroxybenzaldehyde (**H_2L^6**) with 1,3-bis (3-aminopropyl) tetramethyldisiloxane (**AP_0**).



Scheme IV.1. The reaction of formation of **H_2L^{1-6}** azomethine ligands based on salicylaldehyde and its derivatives with 1,3-bis(3-aminopropyl)tetramethyldisiloxane

The second chapter of the original part of the thesis describes the synthesis in a single step and subsequent characterization of compounds prepared with ligands as those described in the previous chapter. The compounds obtained were characterized in terms of structure and also the properties caused by the presence of metal coordinated.



$R^1=R^2=R^3=H$	**CuL^1**
$R^1=R^3=Br, R^2=H$	**CuL^2, NiL^2, ZnL^2**
$R^1=R^3=H, R^2=OH$	**CuL^3**
$R^1=R^2=H, R^3=NO_2$	**CuL^4**
$R^1=R^2=H, R^3=Cl$	**CuL^5**
$R^1=R^3=$*tert*-Bu, $R^2=H$	**NiL^6, CuL^6, $MnL^6(OAc)$**

Scheme V.1. Single stage formation of the coordination compounds on the basis of salicylaldehyde and its derivatives with 1,3-bis(3-aminopropyl)tetramethyldisiloxane

The structures of the obtained complexes were established based on single crystal X-ray diffraction coupled with elemental analysis and spectral (FTIR, ^{1}H NMR and UV) analysis data (*Appendix 1*).

In **Figures V.1**, **V.5**, **V.18** are showed the structures determined for compounds **CuL^1**, **CuL^4** and **CuL^6**. In the thesis are presented in detail the structural and packaging parameters for each of the compounds obtained and their peculiarities.

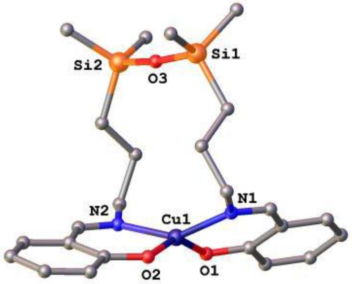


Figure V.1. The molecular structure of the complex **CuL^1** [235]

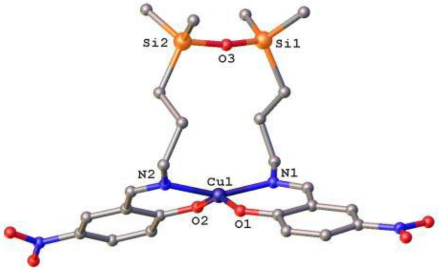


Figure V.5. The molecular structure of the coordinate compound **CuL^4** [235]

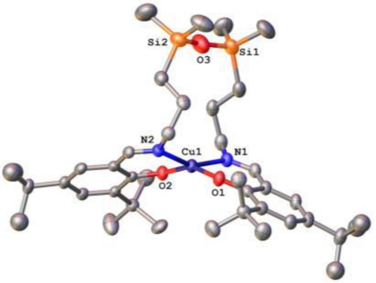


Figure V.18. The molecular structure of the compound of the coordinate **CuL^6** [235]

While most compounds are present as discrete molecules or having weak intermolecular interactions, the compound **CuL^3** complexed with pyridine state **[CuL^3][Cu(4-Me-Py)$_4$Cl]Cl·2H$_2$O** shows a complex 3D supramolecular structure formed by a network of hydrogen interactions O-H···O, O-H··· Cl and C-H···Cl (**Figure V.4**).

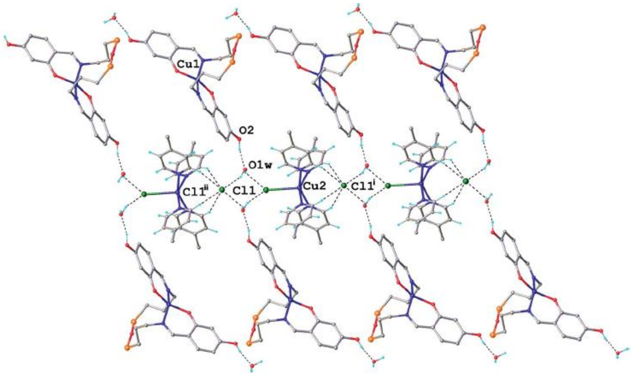


Figure V.4. Fragment of 3D supramolecular network in the crystal structure of the complex **[CuL^3][Cu(4-Me-Py)$_4$Cl]Cl·2H$_2$O** [235]

The complexes **CuL^1**, **CuL^4**, **CuL^2** and **CuL^5** have undergone processes of oxidation/reduction showing redox couples with irreversible character. Cathodic and anodic peak potentials correspond to the reaction of the central metal Cu(II)-Cu(III) and to the oxidation of the phenol/phenoxy central radical in the ligand for Cu(II)-Cu(II)+*. It has been found that, for all the complexes investigated by cyclic voltammetry, the anodic and cathodic peak intensities increase with scan speed, but is always less than unity, indicating that oxidation and reduction processes are quasi-irreversible.

During a special spectroelectrochemistry experiment, coupled with ESR measurements at low temperature, it was measured at 130 K the ESR signal of the **NiL^6** complex oxidized electrochemically, at the first oxidation peak. Obtaining again a rhombic EPR signal indicates the oxidation of the central metal, with the formation of the species Ni^{III} (**Figure V.23**).

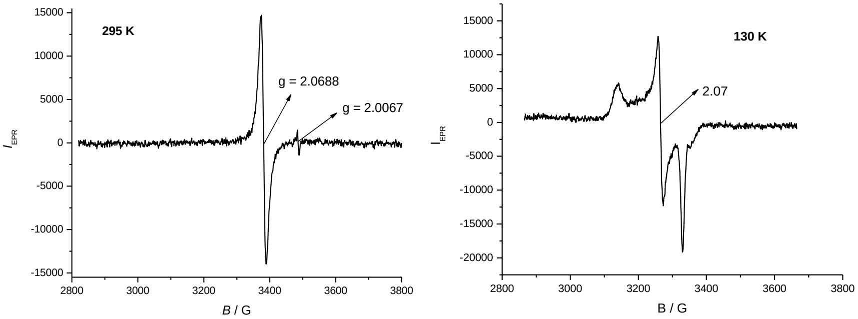


Figure V.23. ESR spectra of NiL$^+$ in TBAPF6/CH$_2$Cl$_2$ measured at 295 K and 130 K [244]

The third chapter of the original part describes the structural and morphology changes induced by the presence of the siloxane blocks in investigated coordination compounds.

VI.1. Structural changes

DFT calculations and experimental analysis of the charge density

The interval in which the angle of Si-O-Si bond varies in the compounds studied (144.4(5)° - **ZnL^2** and 169.75(2)° - **CuL^1**) indicates the lack of strict directionality of the bonds between oxygen and silicon atoms and provides evidence for predominantly ionic nature of the interaction Si-O group dimethylsiloxane.

The optimization of the geometry of compound **CuL^1** has led to a perfect molecular symmetry C_2 with the rotation axis C_2 passing through atoms of Cu and O3. As expected, the bonds optimized by DFT are slightly longer than those estimated by X-ray diffraction (*Table VI.1*). Houser parameter [252] $\tau_4 = 0.265$ (*Table VI.1*) for **CuL^1** structure optimized by DFT (without the influences of solid state) indicates that tetrahedral distortion is not caused by the effects of the solid state and should remain in solution. This is consistent with the tetragonal character of the compound **CuL^1** indicated by ESR spectrum in solution and may explain difficulties in fitting the hyperfine coupling from the ^{14}N of the ligand. The value of the Si-O-Si angle calculated (162.5°) (*Table VI.1*) in the dimethylsiloxane unit, indicating the ionic character of the Si-O bond, is approx. 7° less than the experimental value and this difference can be attributed to solid state effects.

Table VI.1. Comparison of bond lengths (Å) and angles (°) determined experimentally with those obtained from DFT calculations for compound **CuL^1** [235]

	Exp.	Calcd.		Exp.	Calcd.
Cu1-O1	1,882(1)	1,924	**C14-Si2-C13**	110,88(1)	109,9
Cu1-O2	1,886(1)	1,924	**O3-Si2-C15**	107,25(1)	107,5
Cu1-N1	1,960(2)	1,988	**C14-Si2-C15**	107,85(1)	109,5
Cu1-N2	1,963(2)	1,988	**C13-Si2-C15**	111,89(1)	111,2
Si2-O3	1,614(2)	1,658	**O3-Si1-C11**	109,55(1)	109,3
Si2-C13	1,853(3)	1,883	**O3-Si1-C12**	107,86(1)	109,5
Si2-C15	1,854(3)	1,883	**C11-Si1-C12**	110,5(2)	109,9
Si1-O3	1,614(2)	1,658	**O3-Si1-C10**	107,86(1)	107,5
Si1-C11	1,847(3)	1,883	**C11-Si1-C10**	109,62(1)	111,2
Si1-C12	1,853(3)	1,883	**C12-Si1-C10**	111,32(1)	109,5
Si1-C10	1,867(2)	1,890	**C1-O1-Cu1**	127,75(1)	128,6
O1-Cu1-O2	147,77(7)	160,5	**C24-O2-Cu1**	127,67(1)	128,6
O1-Cu1-N1	94,52(7)	91,5	**Si2-O3-Si1**	169,75(2)	162,5
O2-Cu1-N1	95,65(7)	91,5	**C9-C10-Si1**	115,81(2)	115,8
O1-Cu1-N2	93,48(6)	91,5	**C16-C15-Si2**	117,67(2)	115,8
O2-Cu1-N2	94,26(7)	91,5	**C8-N1-Cu1**	118,15(1)	117,0
N1-Cu1-N2	147,28(7)	162,1	**C7-N1-Cu1**	123,77(1)	124,3
O3-Si2-C14	109,48(1)	109,5	**C18-N2-Cu1**	123,79(1)	124,3
O3-Si2-C13	109,40(1)	109,3	**C17-N2-Cu1**	118,05(1)	117,0
τ_{4*}	0,460	0,265			

*) $\tau_4 = \frac{360^\circ - (\alpha + \beta)}{141^\circ}$, where α and β are the two largest angles θ of the Cu atom

VI.2. Morphological changes

Ligands consisting of end-chain bifunctional tetramethyldisiloxane or oligosiloxane and their metal complexes can be regarded as amphiphilic structures in which the strong hydrophobic dimethylsiloxane groups coexist with complexing polar groups or are complexed metal units. Self-assembly of amphiphilic metal-containing complexes involves, besides the interactions found in the organic structures (hydrophobic interactions, host-guest type of interaction, ionic interaction), some specific ones due to the presence of metal which is capable of forming complementary coordinate or metal-metal bonds [283].

Three of copper coordination compounds prepared and characterized as described above, **CuL^1**, **CuL^4** and **CuL^6**, have been selected for such a study . The difference in polarity between the different blocks of the structure of the molecules was estimated based on the theoretical calculation of the dipole moment using known methods [290]. Aggregation of the three complexes in a polar organic solvent (DMF) was studied by surface tension measurements, differential scanning calorimetry in solution, UV-Vis absorption spectrometry, dynamic light scattering (DLS) and small-angle X-ray scattering (SAXS). Conservation of the aggregates in the films formed as a result of slow evaporation of the solvent was examined by transmission electron microscopy (TEM) and atomic force microscopy (AFM).

The surface tension measurements were carried out on solutions of the three complexes in the concentration range of 0.187 to 1.125 g/dl, in DMF at different temperatures. Changes in the values obtained by these parameters are shown for compound **CuL^6** (**Figure VI.8**). These dependencies show similar patterns for the three studied compounds consisting of an alternation of maximum and minimum surface tension that suggests changes in size and shape of aggregates as the concentration changes. But the overall trend is to decrease the surface tension of the solvent (39,939 mN/m) as the concentration increases. For example, for the compound **CuL^1** the surface tension reduces to 31.03 mN/m, for **CuL^4** to 34.87 mN/m, and for **CuL^6** to 26.34 mN/m. Considering the capacity to lower the surface tension as an indicator of surface activity, it can be seen that the best results were obtained with **CuL^6** complex, and its effect is more visible with increasing temperature.

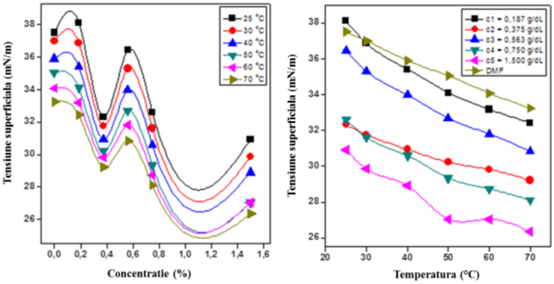


Figure VI.8. Changes in surface tension of compound **CuL^6** in DMF at different temperatures (left) and concentrations (right) [236]

DSC curves recorded in solutions of different concentrations (0.1 and 0.56% in DMF) for each of the three complexes in the same temperature range as in the solid state: -150 - (+100) °C, show the presence of very large endotherms in the range between 20-100 °C (**Figure VI.13**). These are attributed to the destruction of aggregates of various sizes existing in solution, as noted in the literature in similar cases [294]. The values of the enthalpies of these processes correlate well with the structures of these complexes (size of the molecules, the nature of the substituents on the aromatic ring, etc.) these issues being discussed in detail in thesis.

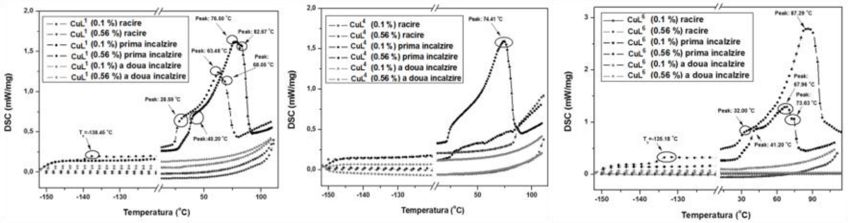


Figure VI.13. Areas of interest of DSC curves recorded in solution (DMF) [236]

Analysis by Small-angle X-ray scattering (SAXS) of **CuL^6** and **CuL^1** compounds in the form of solutions of different concentrations in DMF.The data processing using the SAXS-NT software (Bruker) and ATSAS 2.5.1 allowed to make judgments on the geometry of the aggregates and to estimate their size. For example, for the compound **CuL^1** the shape of the aggregates changes, from that of disc at a concentration of 1% into cylindrical one at a concentration of 7%, the average diameter being between 43 and 56 nm,in dependence on concentration. For compound **CuL^6** the aggregates are transformed from disc-shaped to globular when the solution concentration rises and the maximum diameter is increased from 38 to 50 nm.

The ability to self-assemble in solution was also studied by UV-Vis absorption spectroscopy, dynamic light scattering (DLS), the results and comments on them being detailed in the thesis (see *chap. VI*).

Analysis by microscopic techniques of the supramolecular aggregates

The 7% (weight) solutions analyzed by SAXS were used to prepare films by casting for later TEM analysis. In all cases were obtained nanostructured aggregates, well-defined but with large size polydispersity (**Figure VI.19**).

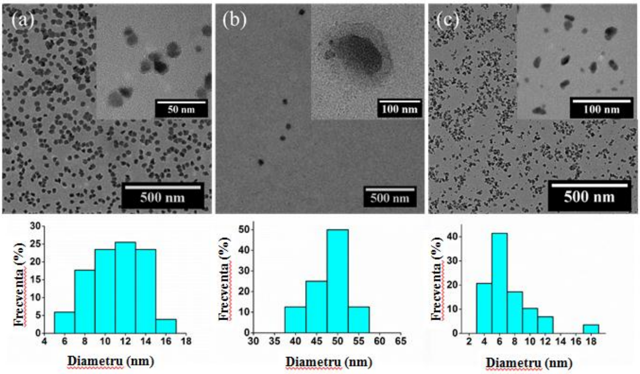


Figure VI.19. TEM images and histograms for: a - **CuL^1**; b - **CuL^4**; c - **CuL^6** as films were cast from drops of 7% (w) in DMF [236]

The sizes of these structures are much smaller (average diameter of aggregates for **CuL^6** and **CuL^1** samples are 11 and 7 nm) than expected based on data collected by SAXS analysis. This difference might be attributable to the effects of the solvent. The aggregates in solution are swollen with large amounts of solvent. Drying of the samples for TEM analysis is carried out by evaporation of the solvent, which is a slow, since DMF has low volatility. During this process, the concentration of the solution increases gradually leading to changes in both morphology and size of aggregates. However, although the aggregates evidenced by TEM are generally smaller than those estimated by SAXS analysis of the solution, they retain their hierarchy by size, the sample **CuL^6** having the smallest aggregates.

Aggregation was also studied by AFM on films prepared by spin-coating, this time with solution concentration of 0.56 g/dL in DMF and with rapid evaporation of the solvent.

AFM images are shown in **Figure VI.20**. In all cases it was observed the formation of irregularly shaped aggregates distributed over the entire scan area. The corresponding images in amplitude mode (**Figure VI.20c and A, B, C**), taken simultaneously with the images in height mode (**Figure VI.20 a, b, A, B, C**) were used to reveal the fine detail of these units. According to the cross-sectional profiles (**Figure VI.20 d, A, B, C**), aggregates were more bulky for sample **CuL^6** than the test sample **CuL^1**. This result reflects the chemical structures of these compounds taking into account the size and the nature of the substituents on the aromatic ring. The form of the aggregates is similar and their appearance suggests there are small crystallites.

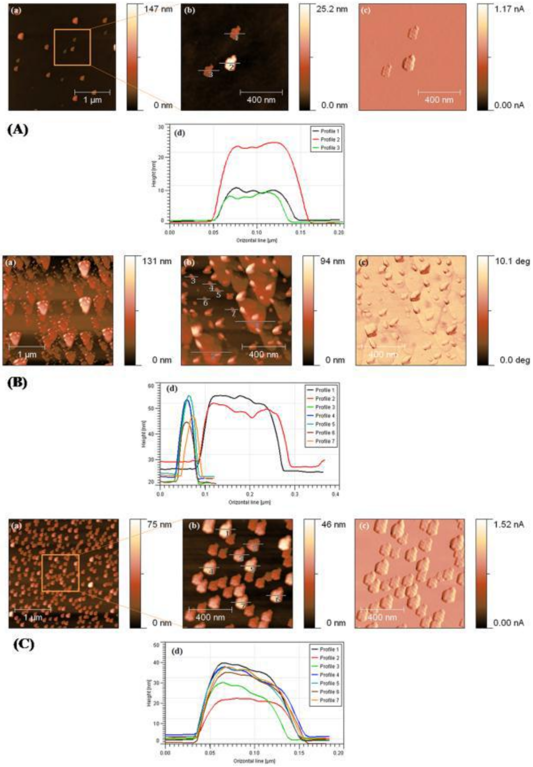
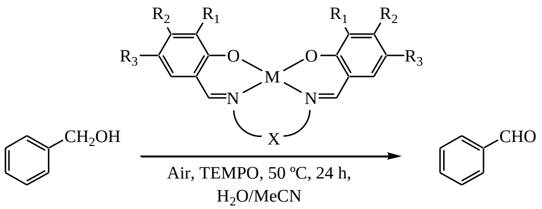


Figure VI.20. AFM measurements made on samples **CuL**^{1} (A), **CuL**^{4} (B) and **CuL**^{6} (C): 2D topographic images with scanning length of 3 mm (a) and 1 µm (b), the amplitude of the image (c) and the cross-sectional profile recorded along the continuous lines in the image (d) [236]

The fourth chapter of the original part of the thesis contains the results of studies on identifying potential applications of coordination compounds obtained.

Starting from the generally known fact that most metal complexes of Schiff bases possess catalyst activity, some of the coordination compounds reported in this thesis have been studied in this regard. The **NiL**^{2} and **ZnL**^{2} compounds were studied from the point of view of catalytic activity in a single model reaction, namely the decomposition of hydrogen peroxide, revealing a good activity of zinc complexes. Another series of compounds (**CuL**$^{1\text{-}5}$) were tested in more complex catalyst reactions, in aerobic oxidation of benzyl alcohol to benzaldehyde mediated by (2,2,6,6-Tetramethylpiperidin-1-yl)oxy (TEMPO) (*Scheme VII.1*).



Scheme VII.1. The aerobic oxydation of benzyl alcohol to benzaldehyde

The results obtained are shown in *Table VII.1* and shows that the studied complexes are effective catalysts, and give a final yield of the reaction of 99% (based on the alcohol) and the number of molecules for the active center (TON) of up to 990 moles of product/mole of catalyst. The system has a high selectivity for the formation of benzaldehyde (over 99%). Control reactions performed in the absence of metal complex or free radical TEMPO indicate that there is no oxidation reaction in any appreciable amounts of alcohol (yield <5%).

Table VII.1. The activity of the complexes of Cu (II) salen type Schiff base in the reaction of aerobic oxidation benzyl alcohol [a] [235]

Nr.	*Catalzst*	*Reaction conditions*	*Yield (%)*[b]	*TON*[c]
1	**CuL^{1}**	MeCN/H$_2$O, 50 °C, 24 h	68,4	684
2	**CuL^{1}**·0,5Py	MeCN/H$_2$O, 50 °C, 24 h	70,6	706
3	**CuL^{2}**·0,375 CH$_2$Cl$_2$	MeCN/H$_2$O, 50 °C, 24 h	83,3	833
4	**CuL^{4}**	MeCN/H$_2$O, 50 °C, 24 h	76,9	769
5	**CuL^{4}**·CHCl$_3$	MeCN/H$_2$O, 50 °C, 24 h	72,1	721
6	**CuL^{5}**	MeCN/H$_2$O, 50 °C, 24 h	85,9	859
7	**CuL^{5}**	MeCN/H$_2$O, 50 °C, 48 h	98,8	988
8	Cu(NO$_3$)$_2$	MeCN/H$_2$O, 50 °C, 48 h	27,5	275
9[d]	Cu(II) complexes of (hydroxyaryl)hydrazo-β-diketones	H$_2$O, 80 °C, 6 h	68	68
10[d]	Multicopper(II) triethanolaminat	H$_2$O, 50 °C, 17 h	47	47
11[d]	Cu(salen)	Toluene, 100 °C, 10 h	99	20
12[d]	self-assembled dicopper(II) diethanolaminate cores	H$_2$O, 50 °C, 4−48h	19−99	19−99
13[d]	Cu(II)- *bis*(3,5-di-tert-butylsalicylaldimine)	Toluene, 100 °C, 3 h	6−78	18−234
14[d,e]	Cu(II)-K coordination polymers	H$_2$O, 80 °C, 18 h	28−67	28−67

[a] reaction conditions: benzyl alcohol (3 mmol), catalyst precursor (3 μmol, 0.1 mol%), TEMPO (0.15 mmol, 5 mol%) in 5 mL of solution 1: 1 MeCN/water of K$_2$CO$_3$ (0.1 mol L -1), 50 °C, air (1 atm) for 24 hours, unless otherwise specified. [b]Moles of product/100 moles of substrate. [c] moles of product/mole of catalyst. [d]For the purpose of comparison, in all cases the selectivity was >99%.

eSelf-assembled from copper nitrate (II), potassium hydroxide and azoderivatives of β-diketones, namely 3-(2-hydroxy-3-sulfo-5-chlorophenylhydrazo)pentane-2,4-dione or 3-(2-hydroxy-3-sulfo-5-nitrophenylhydrazo)pentane-2,4-dione.

The results of the tests for antibacterial and antifungal activity of the test compounds are shown in *Table VII.2*.

Table VII.2. Antimicrobial screening results

	MIC (μg/ml)				
	Fungi			**Bacteria**	
Proba	**Aspergillus flavus ATCC20046**	**Penicillium chrysogenum ATCC 20044**	**Alternaria alternate ATCC8741**	**Bacillus sp. ATCC 31073**	**Pseudomonas aeroginosa ATCC 27813**
	Concentrația probei, wt%				
	2	2	2	2	2
CuL^{5}	0,023	0,023	0,023	2	2
CuL^{4}·CHCl$_3$	0,016	0,016	0,023	2	2
CuL^{2}	0,075	0,075	0,075	1,5	1,5
CuL^{1}	0,19	0,19	0,19	1,0	1,0
NiL·CH$_2$Cl$_2$	>32	>32	>32	>256	>256

$CuL\cdot H_2O$	>32	>32	>32	>256	>256
$MnL(CH_3COO)\cdot H_2O$	2	2	2		
Caspofungin[b]	0,25	0,25	0,25	-	-
Kanamicine[b]	-	-	-	3	3

[b] Standard compound

The biological activity of the copper complexes derived from Schiff base type ligands containing siloxane segment was studied based on the known assumption that the azomethine group, which is polarized more or less due to other groups present in the structure, can form hydrogen bonds with the active center of cell constituents [323]. Organosiloxane fragment confers flexibility and facilitates the interaction of the structure while being biocompatible. The results show that the compounds **$CuL^4\cdot CHCl_3$**, **CuL^5**, **CuL^2** and **CuL^1** showfrom good to very good biological activity, similar to that of the reference compound, Caspofungin and Kanamycin.

The complexes in *Table VII.3* were tested as an additive in the culture biomass of cianobacteria Spirulina platensis in order to increase its antioxidant activity used as 70% ethanolic extract. The results showed an increase in the efficiency of Spirulina extract in classic tests as inhibitor of ABTS.

Table VII.3. The antioxidant activity of Spirulina platensis cianobacteria biomass in the presence of the metal complexes studied

Nr. Crt.	Compounds	Concentration of compound g/L	Antioxidant actvity	
			% inhibiție ABTS	trolox echivalent mg/g
1.	**CuL^5**	0,003; 0,0032	61 ± 1,03 %; 62 ± 1,56 %	Nu s-a determinat
2.	**$CuL^4\cdot CHCl_3$**	2,0	50 – 57	7,0 – 8,0
3.	**CuL^4**	8,0	60 – 63,7	8,0 – 9,0
4.	**CuL^2**	6,0	60 – 69,6	8,0 – 10,0

Active filler to increase the dielectric permittivity of the silicone elastomers

Given the presence in the structure of the obtained complexes of a metal and of a polar component, it is expected that they have high dielectric constant. At the moment there are requirements for dielectric elastomer electromechanical devices (actuators, sensors, energy harvesting, etc.). Silicone polymers are among the most sought for such applications but have the disadvantage that they have low dielectric constant. A simple way to minimize this disadvantage is to incorporate the nanoparticles with high dielectric permittivity as the filler in the matrix of silicon material. Metal complexes obtained in this thesis are an interesting choice because they also contain in their structure the organosiloxanes block which provides compatibility with the matrix. Thus, three compounds were selected and have been incorporated by physically mixing in different concentrations. By incorporating small amounts of these complexes (2-5%) was obtained an increased dielectric permittivity of 3.8 from the value of 3.1 of the matrix.

Conclusions and prospects

The thesis is devoted to obtaining new transition metal complexes based on salen type ligands containing siloxane bond and various metal salts. Based on a rigorous documentation were established lines of research that would allow the production of new coordination compounds and also the study of the effects induced by the presence of siloxane bond on the structure and properties of the compounds obtained in order to add value and contribute to increasing interest in this rather less exploited scientific area.

- Were synthesized six Schiff base type ligands based on a siloxane diamine, 1,3-bis(3-aminopropyl)tetramethyldisiloxane and four salicylaldehyde derivatives in stoichiometric ratios, in solution, at a temperature of 60-70 °C. The reaction products were separated by column chromatography and were characterized by elemental analysis, IR spectroscopy, ^{1}H-NMR and ^{13}C-

NMR and UV-Vis. The absorption bands in IR spectra characteristic for the frequency of vibration of the azomethine group, and the signals characteristic of the movement in ^{1}H-NMR and ^{13}C-NMR spectra confirm the formation of the Schiff bases.

-12 new coordination compounds were prepared with the ligand derived from 1,3-bis(3-aminopropyl) tetramethyldisiloxane (AP$_0$) and various aldehydes: salicylaldehyde (**CuL^1**), 3,5-dibromsalicilaldehidă (**CuL^2**), 2.4-dihydroxybenzaldehide (**CuL^3**), 5-nitrosalicylaldehyde (**CuL^4**), 5-chlorosalicylaldehyde (**CuL^5**) and 3,5-di-tert-butyl-2-hydroxybenzaldehyde (**MnL^6(OAc)**), all of which being isolated as single crystals.

-Two ligands were prepared on the basis of α,ω-bis(3-aminopropyl)oligodimethylsiloxanes having 1,8 and 2,6 extrasiloxane units in comparison with the disiloxane ligands and salicylaldehyde; they formed complexes with a copper salt. Both ligands and complexes were characterized by spectral methods.

-Studies of single crystal X-ray diffraction showed that in almost all the compounds investigated (with the exception of compounds **CuL^3**, **MnL^6(OAc)**), coordinated by a N_2O_2 tetradentate ligand of Schiff base type and leads to the formation of two chelate rings with six members and a chelate ring with 12 members. The compounds **CuL$^{1-5}$**, **NiL^2**, **ZnL^2**, **CuL^6** and **NiL^6** present tetrahedral distorted planar-square coordination geometry. Compared to **NiL^6** and **CuL^6**, the inner coordination sphere of the complex **MnL^6(OAc)** contains, in addition to the tetradentate ligand L^{2-}, an acetate as bidentate-helat ligand. As a result, in the unit of the neutral complex **MnL^6(OAc)** the ion Mn(III) has a distorted octahedral geometry O_4N_2. In the compound **CuL^3** each atom Cu2 has a square-pyramidal coordination geometry provided by the four nitrogen atoms of the ligands 4-Me-Py in the equatorial plane and the chlorine atom in the apical position.

-Siloxane bond angles vary in a very wide range between 169.75(2)° for **CuL^1**, 154.2(3)° for **CuL^4 · CHCl$_3$**, 162.6(6) -164.5(6) for compound **NiL^2** and 144.4(5) -165.6(6) for **ZnL^2** compound, depending on the nature of the substituents on the aromatic ring and the type of metal ion.

-DFT calculations indicate no strict directionality Si-O bond and provide evidence for predominantly ionic nature of it.

-The measurements of surface tension of the Schiff base type ligands and complexes containing organosiloxanes spacers and their metal derivatives have shown that they exhibit surface activity with the possibility of aggregation in solution. The biggest decrease of the value of surface tension as compared with that for the solvent (39,939 mN/m for DMF) was observed in the case of organosiloxanes **O2R1** ligand - 29,974 mN/m, and in the case of its complex, **O2R1Cu** - 26,313 mN/m. The decrease of this parameter's value has accentuated with increasing siloxane segment length in both the ligands and the complexes showing the significant effect of the siloxane component on the morphology compounds that were the subject of the thesis.

-The formation of aggregates in solution, and their size was estimated based on DLS and SAXS studies in solutions of different concentrations. While DLS analysis indicates the presence of polydisperse aggregates with 1-2 populations, SAXS analysis the mean diameter of the aggregates estimated by SAXS analysis were in the range 38-56 nm, depending on the nature and concentration of the sample. Their conservation in the film formed by casting after evaporation of the solvent was evidenced by TEM, but was found a decrease in their size compared with those identified in solution due to the continuous change of the concentration of the solution during solvent evaporation; this causes conformational and dimensional rearrangements of the aggregates. The aggregates emphasized on films obtained by spin-coating are similar in size to those estimated by DLS in solution. When larger siloxane segments are present in the structure, the aggregates have a well-defined shape.

-The salen type Schiff base complexes of copper (II) containing a disiloxane fragment, in particular those with electron-withdrawn substituents (chlorine, bromine and nitro) on the aromatic ring, have a high catalytic activity and selectivity for aerobic oxidation of the benzyl alcohol to the aldehyde, mediated by the radical TEMPO in mild conditions (aqueous acetonitrile at 50 °C, a more environmentally friendly solvent than the pure organic solvents).

-The compounds **CuL^4**, **CuL^5**, **CuL^2** and **CuL^1** showed a very good and good biological activity, similar to that of reference compounds considered, Caspofungin and Kanamycin.

-The compounds **CuL^2**, **CuL^4** and **CuL^5** have been shown to be useful in biotechnology in the cultivation of Spirulina platensis, increasing its antioxidant activity.

-The compounds **M_1L**, **M_2L**, and **M_3L** (1 – Mn, 2 -Fe, 3 - Cr) have been shown to be active fillers for improving the performance of electroactive polymer (dielectric elastomers).

Prospects

-Expanding the range of ligands and their coordination compounds by using carbonyl compounds and metals that induce or potentiate some properties for target applications (catalysis, magnetism, optics, biology, etc.);

-Testing the catalytic activity for a broad range of reaction and systems types;

-Extending studies on the potential applications of these compounds for optics, magnetism, biology.

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2. *A supramolecular structure based on copper complex of 2,3-pyridinedicarboxylic acid and 1,3-bis(3-aminopropyl)tetramethyldisiloxane chlorohydrate*, **Soroceanu**, **A.**; Bargan, A.; Shova, S.; Cazacu, M. *J. Molec. Struct*. **2014** - revised manuscript.

3. *Nickel(II), Copper(II) and Manganese(III) Complexes with a Schiff Base Containing a Disiloxane Unit: Synthesis, Structure, Spectroelectrochemical Properties and DFT Calculations*, **Soroceanu**, **A.**; Cazacu, M.; Shova, S.; Machata, P.; Breza, M.; Rapta, P.; Telser, J.; Arion, V. B. - manuscript.

4. *Siloxanes with metal complexes yield elastorms with improved dielectric properties*, **Soroceanu**, **A.**; Ştiubianu, G.; Musteaţă, V.; Bele, A.; Cazacu, M.; Vărgănici, C. - manuscript.

5. *The influence of the molecular mass of polydimethylsiloxanes on dielectric properties of composites with metal complexes*, Ştiubianu, G.; **Soroceanu**, **A.**; Musteaţă, V.; Bele, A.; Cazacu, M.; Vărgănici, C. – manuscript.

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Oral communications

1. *Structura moleculară pe baza complexului de cupru al acidului 2,3-piridindicarboxilic şi a clorhidratului de 1,3-bis(3-aminopropil)tetrametildisiloxan*, **Soroceanu**, **A.**; Bargan, A.; Shova, S.; Cazacu, M. A XXIV-a sesiune de comunicări ştiinţifice a Institutului de Chimie Macromoleculară „Petru Poni”, Iaşi, 3 - 5 octombrie 2013.

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1. *New complexes of Cu(II) with salen type ligands containing siloxane segment. Synthesis and structural characterization*, **Lazar**, **A.**; Shova, S.; Turta, C.; Cazacu, M. *A XXIII-a sesiune de comunicari stiintifice a Institutului de Chimie Macromoleculara „Petru Poni”*, Iasi, 29 Septembrie - 1 Octombrie 2011.

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