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CHEMISTRY field

COORDINATION COMPOUNDS OF DIFFERENT DIMENSIONALITY WITH LIGANDS CONTAINING SILOXANE SPACERS

SUMMARY OF DOCTORAL THESIS

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"Petru Poni" Institute of Macromolecular Chemistry

Mrs./Mr. ....

We inform you that on **12th of December 2023, 12^{00}**, in **Conference Hall of the Institute of Macromolecular Chemistry "Petru Poni"**, Iasi, will take place the public presentation of the doctoral thesis "Coordination compounds of different dimensionality with ligands containing siloxane spacers", author **Alexandru-Constantin Stoica**, in order to confer the scientific title of doctor.

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In accordance with the Regulations on the organization and PhD defense within the Romanian Academy, we send you the summary of the doctoral thesis with the kind request to communicate your appreciations and observations. On this occasion, we invite you to participate in the public defense of the doctoral thesis.

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TABLE OF CONTENT

I. INTRODUCTION

I.1. The context and motivation for choosing the research topic

In the modern era, silicon and derived compounds have enabled the development of materials of interest, from the field of computers - silicon underpinning many electrical and electronic components - to aerospace thus helping to shape the technology of the 20th and early 21st centuries. On the other hand, the demands of new technologies stimulated the rapid development of silicon chemistry as part of the "renaissance" of inorganic chemistry [2]. The beginning of research in the field of silicon chemistry dates back to the 20th century, when the first silicon-based compounds were considered "miracle compounds" and continued to develop continuously, receiving great attention from the scientific community and beyond. The increased interest in this field results from the special characteristics and versatility of silicon-based compounds, which can be designed to meet the most demanding requirements for target applications in various fields, such as electronics (transducers, processors), optics (lenses, contact lenses), automotive (vulcanized rubbers, gaskets, hoses), medicine (various medical devices and implants), space (gaskets, coatings), etc. Taking into account the demonstrated performances and the potential for diversification that this class of compounds and materials presents, a strong motivation has been created for further research in this field, which would allow the widening of the range of properties and uses.

At the same time, silicon is also found in coordination compounds. Coordination compounds in general enjoy great interest from the scientific community due to their varied properties and potential applications in a wide range of fields, including supramolecular chemistry, catalysis, medicinal chemistry, and materials technology. The coordination ability of silicon has attracted the attention of researchers in the field, who have developed a wide range of sophisticated complexes with hypervalent (penta-/hexa-coordinated) or low-valent silicon, addressing new synthetic methodologies, structural elucidations, bonding analyzes and possible applications in catalysis or chemical transformations. The coordination chemistry of low-valent silicon-containing ligands has been established as an independent, rapidly expanding field of research. A major discovery was that of stable coordination compounds of silylenes. The use of disilanes allows access to a new class of ligands with increased basicity [3,4].

I.2. The importance, novelty and topicality of the theme

A way to exploit the peculiarities of the siloxane bond in coordination compounds is to include them as fragments in the structure of some ligands with common coordination groups (-COOH, -CN, -C=N-, etc.), which was also addressed in the present thesis. It is a direction with a high degree of originality and there aren't many reports on this approach in the literature. The reason might be the sensitivity of the siloxane bond to several metal salts, to strongly acidic or basic environments, when the syntheses impose such conditions, or the extreme flexibility of this fragment, which is not favorable to the assembly and stabilization of the compounds in organized structures suitable for crystallographic analysis, which is a great challenge for such compounds. Performing a query for the Si-O-Si fragment in the *CCDC* database, version 5.43 – updated at the end of 2022, a number of 3487 results were obtained (including 232 structures with a bis-(methylene)tetramethyldisiloxane fragment), consisting mainly in inorganic or organosiloxane and coordination compounds. More than 60 of these are coordination compounds that were registered by the ICMPP group after 2010. The small number of such structures (compared to 122276 structures found after "ethylenediamine" fragment, for example) confirms the difficulty of their isolation and characterization.

Despite these limitations, the introduction of the siloxane bond, more precisely the tetramethyldisiloxane fragment, through its pronounced flexible and hydrophobic character, in contrasting coexistence with the rigid and polar coordination blocks, creates premises for the manifestation of the amphiphilic character with specific implications in all the properties of the resulting compounds, which differ significantly from analogues based on totally organic ligands. The development of such research involves the chemistry of organosilicon compounds. Thus, the use of siloxane ligands for the complexation of metal ions constitutes a relatively recent approach in coordination chemistry, the existing results mainly belonging to the group in which this thesis was developed and can bring an innovative perspective on this field.

I.4. Formulation of the research hypothesis

The proposed topic aims to enrich the class of coordination compounds, which contain the tetramethyldisiloxane fragment in the structure, with new representatives consisting of coordination compounds of different dimensions, from small molecular compounds (0D) to 1D-3D coordination polymers using as ligands commercially available compounds or derivatives containing this structural motif and differing by the coordination group (-COOH, -C≡N, -HC=N-). Pyridyl derivatives (4,4′-ethylenedipyridyl and 4,4′-azopyridine) were used as co-ligands to direct the structures. As metal species, Mn, Co, Ni, Cu, Zn and Cd were selected based on the already proven wide applicability of their complexes with conventional, organic ligands. In combination with the organic-inorganic ligands addressed in the thesis, it is expected to obtain specific properties induced by the latter.

I.5. Scientific objectives

To achieve the thesis, the following objectives were established:

- obtaining coordination compounds of different dimensions by the appropriate choice of ligand and metal, their ratio and reaction conditions;
- the experimental and theoretical study of the chemical reactivity of the ligand and how this is reflected in the reaction products;
- structural characterization of the obtained compounds (elemental, spectral, crystallographic analysis);
- identifying the outstanding properties of the obtained compounds (optical, thermal, electrical, surface);
- tests of applied utilization of the compounds obtained, alone or in mixed systems (composites based on silicone matrix).

I.6. Brief presentation of the content of the work, emphasizing the results obtained

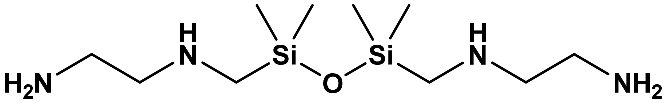
The doctoral thesis is structured in two parts: the first one includes the second chapter, in which are presented data from the literature that support the proposed research, while the second part, consisting in the third chapter, is dedicated to the original contributions, which mainly refer to obtaining four classes of compounds differing in their dimensionality. Thus, in ***Subchapter III.1.*** derivatization reactions of a siloxane diamine, 1,3-bis(2-aminoethylaminomethyl)tetramethyldisiloxane, are presented, with the study of the obtained 0D compounds and the reaction mechanism leading to their formation. ***Subchapter III.2.1.*** shows the preparation of 1D coordination polymers. Nine new polymers were synthesized, isolated in the crystalline state, and structurally characterized. A silico-organic compound, 1,3-bis(cyanopropyl)tetramethyldisiloxane, which is commercially available but has not been used for this purpose so far, was used as a ligand. The same ligand was also used to obtain two 2D coordination polymers that are the subject of ***Subchapter III.2.2.1.*** It has been observed that by changing the nature of the counterion, different architectures and a new network topology can be obtained. A third 2D coordination polymer was obtained as a byproduct in the complexation reaction of cadmium with a mixture of two ligands, namely 1,3-bis(carboxypropyl)tetramethyldisiloxane and 4,4′-azopyridine, from where it was separated with success, phase purity being demonstrated by X-ray powder diffraction. Also, based on the synthesized coordination polymers, a series of composite materials were prepared. The dielectric, mechanical and stimulus responsive properties of the materials were investigated.In ***Subchapter III.2.2.2.*** syntheses were performed to obtain 3D coordination structures using mixtures of ligands: 1,3-bis(carboxypropyl)-tetramethyldisiloxane with 4,4′-ethylenedipyridyl and 4,4′-azopyridine, respectively. These are the first ligand-constructed 3D MOFs containing siloxane spacer reported by our group. The compounds were structurally characterized, and their properties and potential application were studied. Further, these compounds were incorporated as fillers in PDMS matrices, the resulting composite materials being tested for possible applications.

In ***Subchapter III.2.3.*** the synthesis of two new proligands, derived from silsesquioxanes, which were used for the complexation of Ni^{2+}, Cu^{2+} and Cd^{2+} from aqueous solutions is presented. The newly formed complexes were tested to determine their catalytic activity in the decomposition reactions of hydrogen peroxide and the photodegradation of Congo red dye.

III. ORIGINAL CONTRIBUTIONS

III.1. 0D coordination combinations with ligands containing the siloxane bond

Following up on the team's research on coordinative combinations with ligands based on 1,3-bis(3-aminopropyl)tetramethyldisiloxane, in this thesis, it was intended to broaden these classes of compounds, by using another diamine as a siloxane fragment carrier, that is 1,3-bis(2-aminoethylaminomethyl)-tetramethyldisiloxane (SFA) (Scheme 8). This diamine is commercially available with a degree of purity of 95%, the only reported use for it so far being as a curing agent for epoxy resins [202,203] or for CO_2 retention [204].



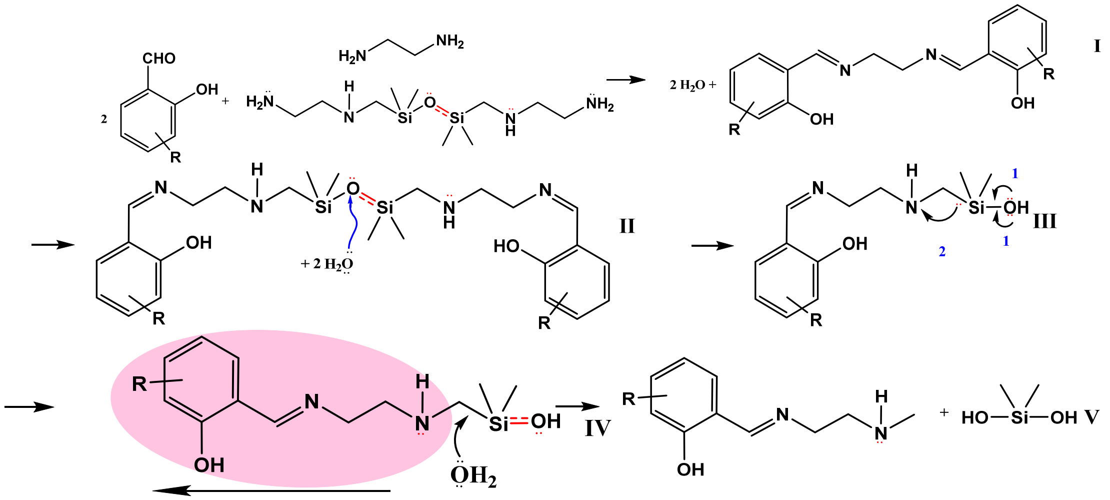
Scheme 8. 1,3-bis(2-aminoethylaminomethyl)tetramethyldisiloxane (SFA)

It would be expected, that the secondary amine groups to perform supramolecular interactions, at the very least that will contribute to the strengthening of the crystal structure. However, since during the implementation of the experimental synthesis program based on this compound, other reactions than expected ones occurred, it was considered necessary to study the reactivity of this compound and the mechanism and conditions under which its fragmentation occurs.

III.1.2. Iminization reaction of SFA, reaction mechanism and structural evidence

After several attempts to obtain derived Schiff bases, it was concluded that this diamine is unstable in the reaction medium, and based on the structures formed, an attempt was made to explain this instability and propose a reaction mechanism (Scheme 18).

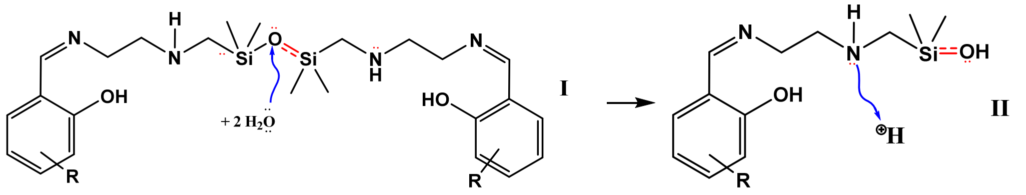
According to Dankert and Hänisch [5], there are two types of vicinal hyperconjugation interactions in siloxanes. The first involves the 2*p* electrons of oxygen, which interact with the 3*d* orbital of silicon, i.e. *p*(O) → *d*(Si). The second type involves the 2*p* electrons of oxygen interacting with the σ*(Si-R) virtual molecular orbital, i.e. p(O) → σ*(Si-R). Both types of interactions are known as "*back-bonding*". These vicinal hyperconjugation interactions can also cause competition between electron donation to electrophiles and stabilization of the Si–O bond. Previous studies have pointed out that both *p* → *d*(Si) and *p*(O) → σ*(Si-R) interactions are simultaneously present in siloxanes. In this case, the presence of the nitrogen atom in the *β* position, i.e. within the R residue (R = $-CH_2-NH-$), has an influence on the hyperconjugation interaction, *p*(O) → σ* (Si-R), which leads to the destabilization of the Si-O bond.

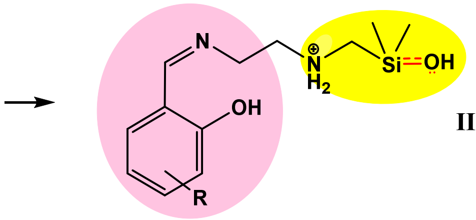


the displacement of the electron cloud towards the benzene nucleus

Scheme 18. Proposed mechanism for the cleavage of SFA amine in the reaction with carbonyl compounds

According to the proposed mechanism (Scheme 19), by protonating the mono-Schiff base at the secondary amino nitrogen, two electronic regions are formed, thus stabilizing the silanol bond.





III

Scheme 19. The proposed reaction mechanism in acidic medium

A series of attempts were made to obtain crystalline structures using SFA. However, during the implementation of the experimental program, a series of compounds (organic compounds or complexes) were obtained in which diamine cleavage was observed. The only case in which silicon was preserved (in the form of a silanol group) is complex **a1**, the other structures obtained in various stabilization attempts leading to the formation of totally organic ligands and their complex combinations, respectively. Experimental data and mechanism premises are supported by theoretical calculations. The main structures obtained, which demonstrate the hypotheses of the mechanism, are presented in Figures 15-17. Thus, in the category of 0D complexes, based on silicon-containing ligands, only the **a1** complex is part, a complex used further for the functionalization of a glass plate.

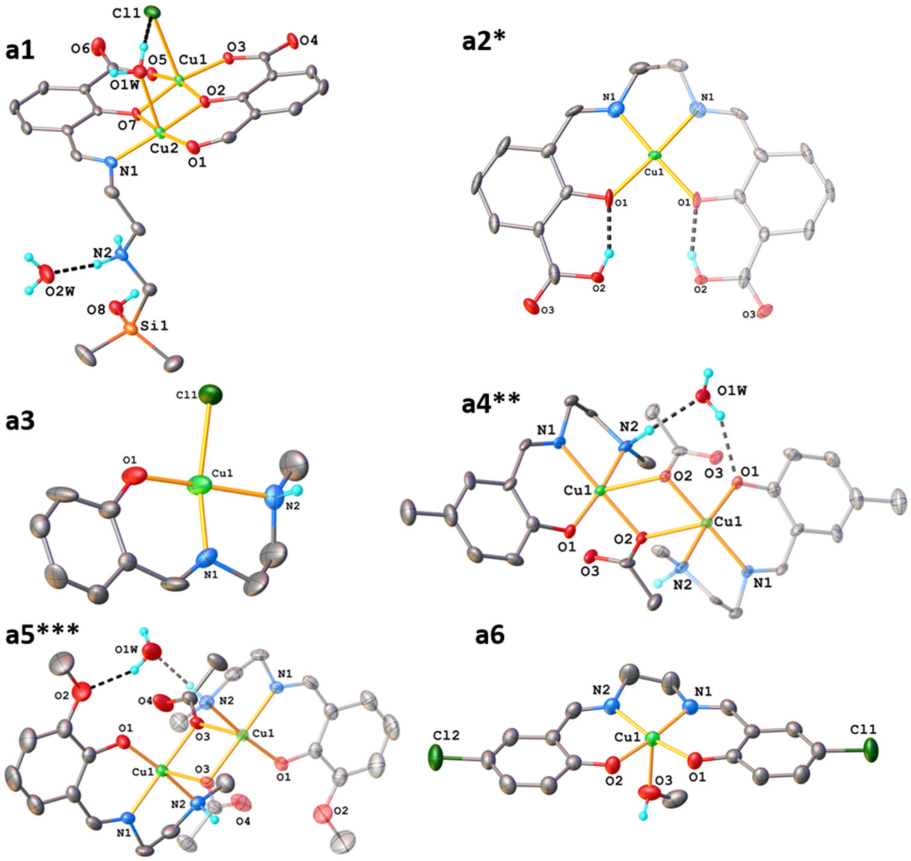


Figure 15. SC XRD analysis for compounds ***a1-a6*** *(symmetry code: *- 1 − x, + y, ½ − z, **- 1 − x, 2 − y, 1 − z; ***- 1 − x, 1 − y, 1 − z). No. CCDC: a2: 818612, [207])*

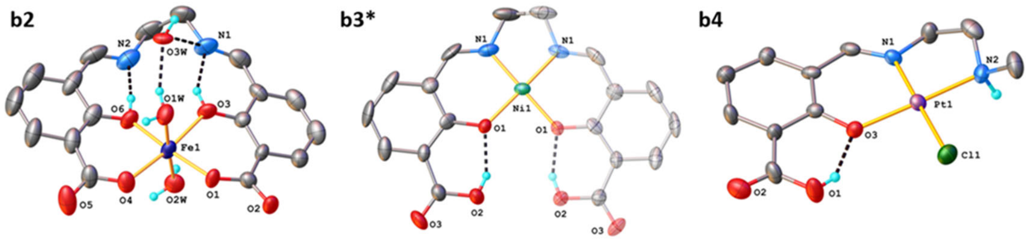


*Figure 16. SC XRD analysis for compounds **b2-b4** (symmetry code: *- 3/2 − x, + y, 1 − z)*

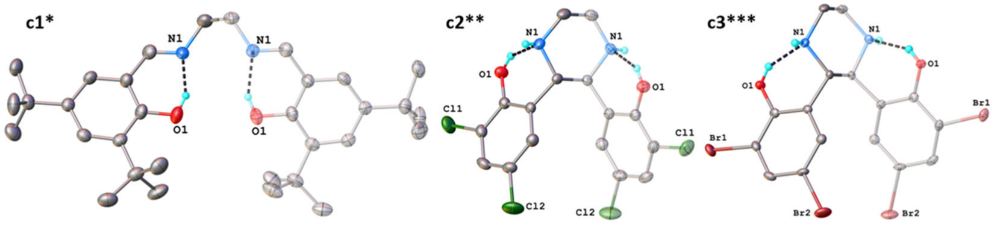


*Figure 17. SC XRD analysis for compounds **c1-c3** (symmetry code: *- 1 − x, + y, ½ − z (No. CCDC: 102872, 253998, [208]); **- 3/2 − x, + y, 1 − z; ***- ½ − x, + y, 1 − z)*

III.2. Coordination polymers (PC)

The investigation on coordination polymers is emerging, due to their electronic, magnetic and porosity properties. They also benefit from the possibility of fine-tuning the properties through the wide variety of organic ligands and direct chemical functionalization possibilities. In this chapter, complexes obtained by using the organo-silico ligand, 1,3-bis(cyanopropyl)tetramethyldisiloxane (***Cy***), which is commercially available but has not been used for this purpose, are reported. By reacting it with melts of metal salts (metal perchlorates) a series of 1D coordination polymers (**PC-1÷6**) were obtained. A 1D coordination polymer was also obtained using copper benzoate as a metal ion carrier (**PC-7**). Two other new 1D coordination polymers (**PC-8**, **PC-9**) were obtained using a double ion-exchange reaction..

III.2.1.2. Structural characterization of 1D coordination polymers

For the series of coordination polymers based on 1,3-bis(3-cyanopropyl)-tetramethyldisiloxane with Mn^{2+}, Zn^{2+} or Cd^{2+} perchlorates (**PC-1÷3**), SC XRD analysis revealed that the three coordination polymers are isostructural, the asymmetric unit being constituted by a ***Cy*** molecule, a metal ion, four coordination H_2O molecules and two perchlorate anions, $\{[MCy(H_2O)_4](ClO_4)_2\}_n$. The metal atoms occupy a special position that coincides with the position of the inversion center. The surrounding of the metal is octahedral, slightly distorted, the base of the octahedron being made up of four coordination water molecules, and in the axial position there are two N atoms from ***Cy***, the ligand acting as a bridge (Figure 40).

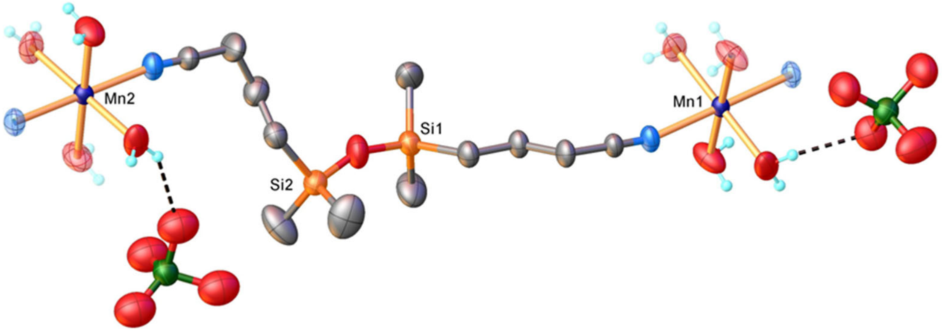


*Figure 40. The asymmetric unit of **PC-1÷3** complexes*

The results of dynamic water vapor sorption capacity (DVS) analysis revealed that compared to the ligand (which has a sorption capacity of 1.7%), the obtained complexes are hydrophilic (Figure 43).

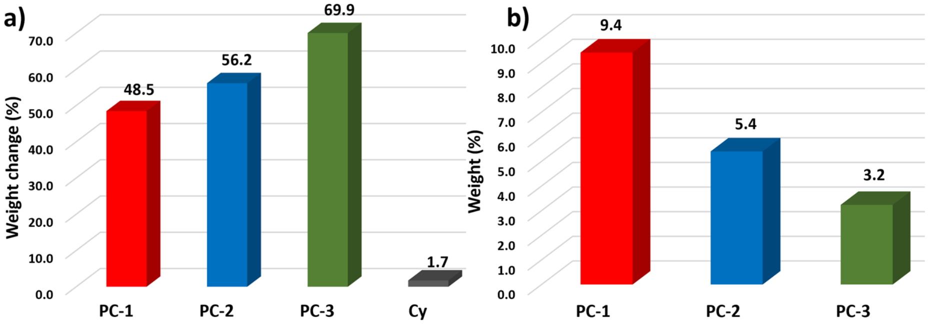


Figure 43. DVS analysis: a – maximum percentage of absorbed water, b – percentage of residual water after desorption

A special case is the copper(II) complex ($[CuCy(H_2O)_2(ClO_4)_2]_n$), in which the metal ion presents a distorted pseudo-octahedral surround of the 4+2 type. The perchlorate anion pseudo-coordinates to the Cu atom (Cu-O 2.48(16) - 2.5(16)) in the apical position, and two coordination water molecules and two N atoms are in the equatorial position (Figure 44).

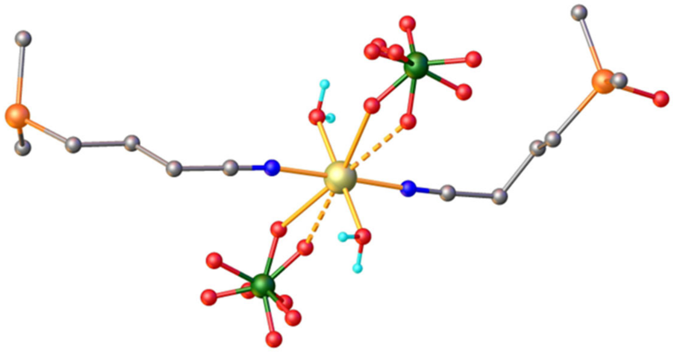


*Figure 44. The asymmetric unit of the **PC-4** complex*

X-ray diffraction analysis demonstrated the isostructurality of the compounds based on ***Cy*** and Fe^{2+} or Co^{2+} (**PC-5**, **PC-6**), having similar unit cell parameters. Their crystal structure is made up of molecular $[Cy_2Fe(H_2O)_2]^{2+}$ and polymeric cations $[CyFe(H_2O)_2]_n^{2+}$ (Figure 45 – exemplified for PC-5) and ClO_4^- anions in a molar ratio of 1:1:4.

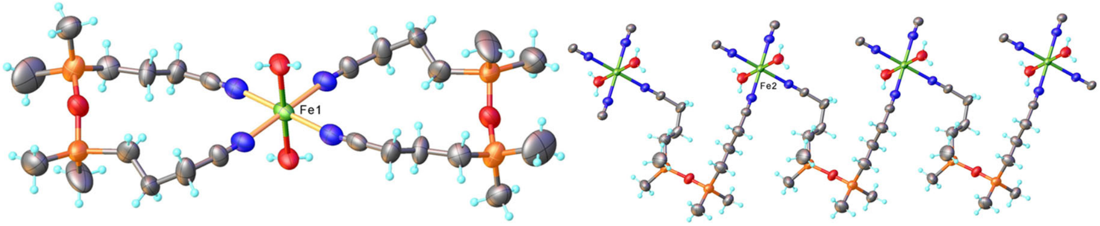


*Figure 45. X-ray structure of **PC-5** complexes (similar for **PC-6**); unit of small molecular structure and 1D polymer chain*

The SC XRD analysis for **PC-7** reveals the formation of a *zig-zag* shaped 1D coordination polymer. The network nodes are formed by $M_2(COO)_4$ "*paddle wheel*" dimers. Each metal atom shows a slightly distorted pyramidal-square type surround (characteristic for such compounds), consisting of four carboxylic O atoms at the base of the pyramid and two N atoms at its top (Figure 47). The supramolecular structure consists of chains overlapping at an angle of approximately 90º, the layers being made of 1D chains arranged parallel to each other.

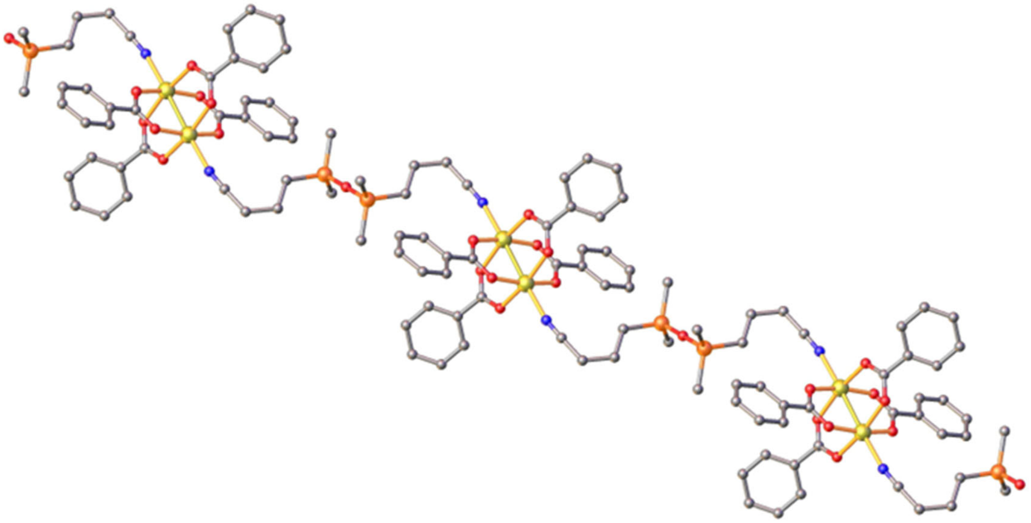


*Figure 47. Fragment of the coordination polymer **PC-7***

SC XRD analysis for coordination polymers **PC-8** and **PC-9** with ***Cy*** ligand, revealed that the coordination polymers are isostructural, the asymmetric unit being formed by half molecule of ***Cy***, a metal ion, two molecules of coordination H_2O, an iodide anion, and a co-crystallizing H_2O molecule. The metal's surrounding is octahedral, slightly distorted, the base of the octahedron being made up of four coordination H_2O molecules, and in the axial position are the two N atoms from ***Cy***, the ligand acting as a bridge (Figure 49 – exemplified for **PC-8**). In both cases, the metal atoms are in a special position that coincides with the inversion center.

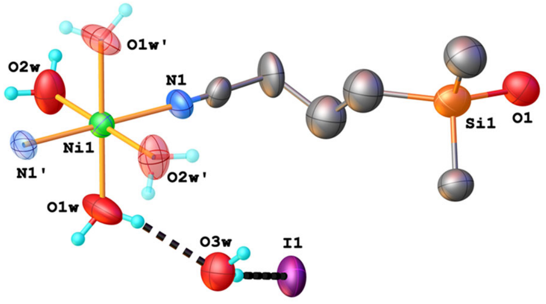


Figure 49. The asymmetric unit of coordination polymers ***PC-8****,* ***PC-9****. Symmetry code ') 1 – x, 1 – y, 1 – z*

The crystalline structure is made up of a 1D cationic polymer chain, the charges being counterbalanced by the presence, in the vicinity of the metal centers, of two iodide anions. The supramolecular structure is determined by the hydrogen bonds that form between the anion, coordination H_2O and the co-crystallization H_2O molecules. In all cases, ***Cy*** exhibits a transoid spatial configuration (Figure 50).

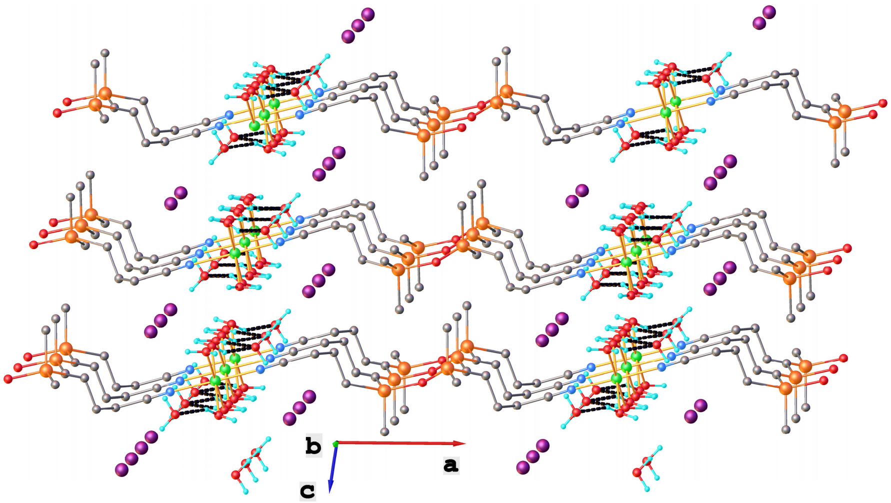


Figure 50. Supramolecular structure of coordination polymers ***PC-8****,* ***PC-9***

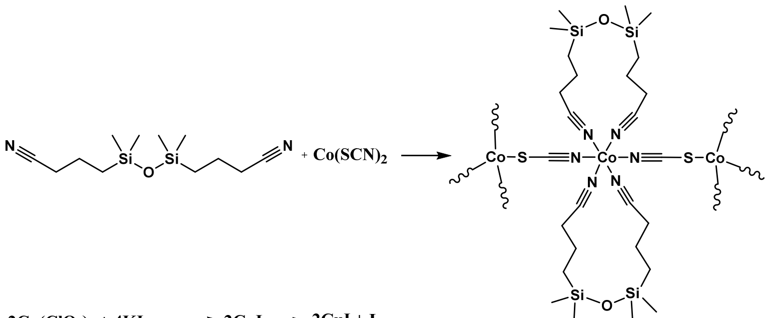
III.2.2. Coordination networks

In general, using a 1:1 ligand:metal ratio can lead to the obtaining of 1D polymer chains, while by changing the stoichiometry, increasing the ligand:metal ratio, the formation of two- or three-dimensional coordination networks is favored. The presence and nature of auxiliary ligands or counterions can also favor the formation of 1D coordination polymers, or 2D and 3D networks [222].

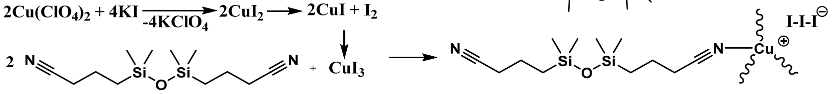
III.2.2.1. Polymers or 2D coordination networks (PC 2D)

The possibility of expanding the space between 2D layers induced by guest molecules and favored by weak interactions such as van der Waals interactions, ion-dipole forces, hydrogen bonds and dipole-dipole attractions make 2D topological networks reasonable prototypes for access and storage selectivity of guest molecules. The volume and polarity of adsorbed target molecules can be a significant factor in the exchange of "*guest*" molecules in porous crystalline "*hosts*" [224].

Within this thesis, two 2D coordination polymers were synthesized, based on ***Cy*** and cobalt thiocyanate and copper triiodide, respectively (Schemes 22-23).



*Scheme 22. Reaction to obtain the **PC-10** polymer*



*Scheme 22. Reaction to obtain the **PC-11** polymer*

III.2.2.1.2. Structural characterization of 2D coordination polymers (PC-10, PC-11)

The SC XRD analysis for **PC-10** polymer, revealed that the asymmetric unit is constituted by two metal centers and a ***Cy*** (in a cisoid form) ligand that coordinates to a Co atom. The Co1 atom with octahedral surrounding occupies a special position that coincides with the inversion center, and the Co2 atom (tetrahedral surrounding) occupies a general position. Also, three thiocyanate groups are present in the asymmetric unit. The ***Cy*** ligand coordinates to the Co1 atom, occupying the equatorial positions, and the thiocyanate counterion occupies the apical positions. The interaction between the Co1 and Co2 atoms is achieved through a thiocyanate bridge (Figure 51).

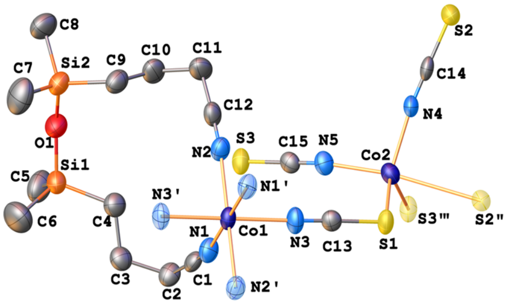


*Figure 51. Asymmetric unit of **PC-10** polymer; Symmetry code: ')1 – x, 2 – y, – z '')2 – x, 2 – y, 1 – z ''')1 – x, 2 – y, 1 – z*

Self-assembly of the asymmetric unit leads to the formation of a 2D coordination polymer, of the $\{CoCy_2[Co(SCN)_4]_2\}_n$ type, electrically neutral (Figure 52).

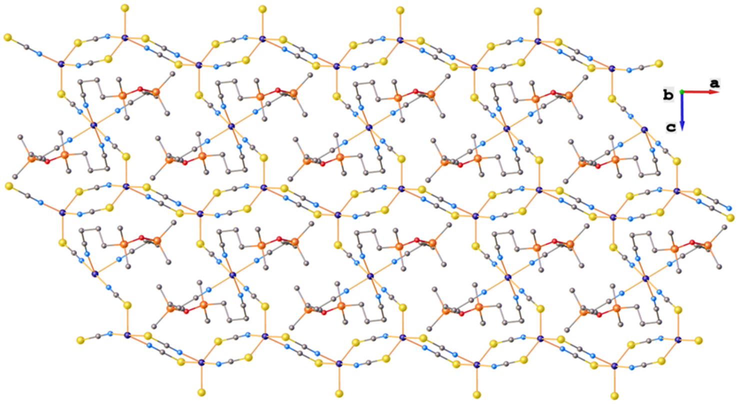


*Figure 52. 2D structure of coordination polymer **PC-10***

The PC-10 compound was analyzed by the DVS technique, the results showing a maximum water absorption capacity of 32.0 wt% at a relative humidity of 80%, and a residual water content after desorption of 2.6 wt%.

According to the SC XRD analysis data, the **PC-11** compound has a 2D polymer type structure, $\{[Cu(Cy)_2]I_3\}_n$, with the ***Cy*** fragment showing a cisoid conformation (Figure 55).

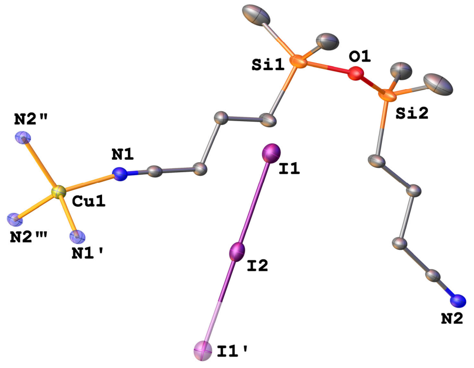


Figure 55. Asymmetric unit of PC-11. Symmetry codes: ')1 – x, + y, 3/2 –z; ")+ x, – 1 + y, 1 + z ''')1 – x, –1 + y, ½ – z

Self-assembly of the asymmetric unit, in the crystal, leads to the formation of a 2D coordination polymer $\{[Cu(Cy)_2]I_3\}_n$. The network of the 2D polymer is of 4+2 type, with the Cu atom acting as a network node and the ligand acting as a bridge (Figure 56). The crystal structure results from the parallel packing of the 2D layers, through Van der Waals interactions between the layers (Figure 57), the interlayer distance (calculated as the $Si\text{-}CH_3\text{-}Si\text{-}CH_3$ distance) being 3.004(10) Å. The experimental diffractogram mimics the simulated diffractogram based on SC XRD analysis, which confirms the purity of the compound.

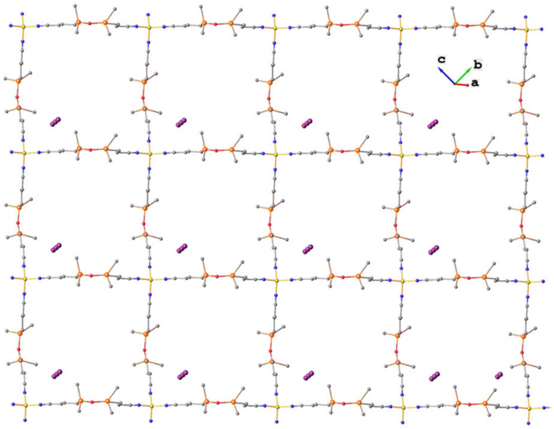


*Figure 56. Planar-square network of coordination polymer **PC-11***

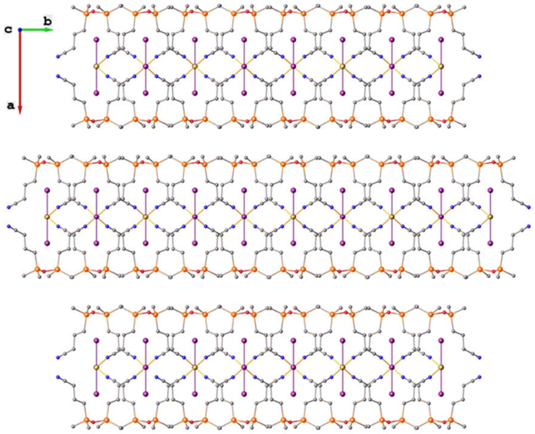


*Figure 57. Crystal structure of polymer **PC-11***

III.2.2.1.3. Delamination of 2D compounds (PC-10, PC-11) and characterization of nanosheets

To take full advantage of the properties of a 2D material it has to be delaminated. Delamination, in the ideal case down to an atomic monolayer, gives the 2D material the lowest possible thickness-to-surface ratio, which leads to a large number of active centers on the surface of the material. By delamination of 2D coordination polymers, an increase in their properties can be ensured, such as for example a higher catalytic activity, retention of electronic charges or ions, etc. Considering the weak interactions between the 2D layers of these compounds, both chemical intercalation and solvent ultrasound can be used as delamination methods. To have the most efficient delamination, the combination of these two methods was resorted to, namely the intercalation of some THF molecules between the layers of the compounds, assisted by ultrasound. The resulting suspension was embedded in a PDMS matrix to prevent restacking of the nanosheets. The film thus obtained was analyzed by the SEM-EDX technique (Figure 66).

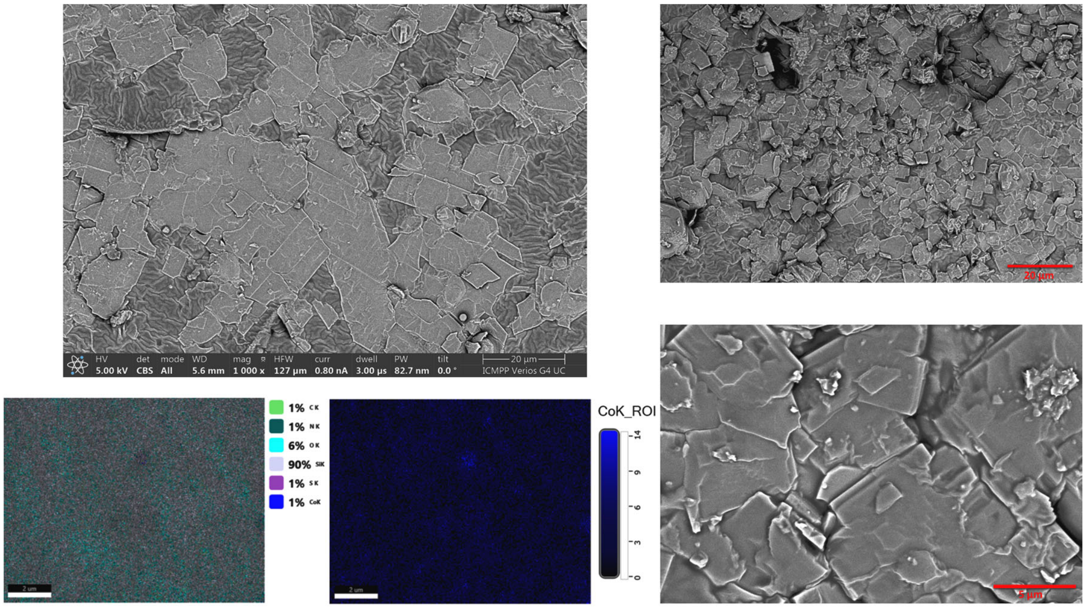


*Figure 66. SEM images of the composites with **PC-10** filler, respectively the map of the distribution of elements in the material*

III.2.2.1.5. Characterization of composite materials (MC-1÷6)

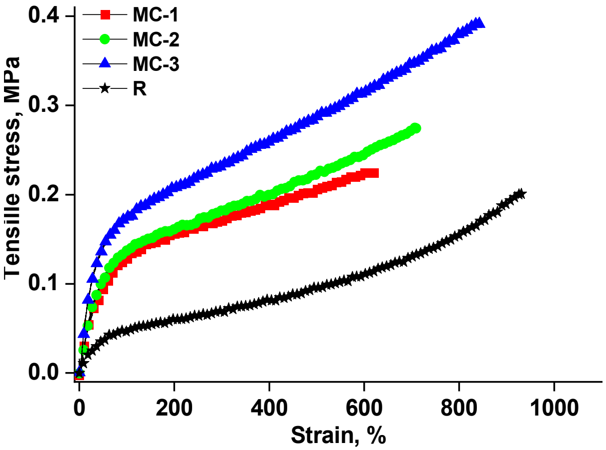


*Figure 67. Stress-strain curves for MC composites with **PC-10** filler compared to the sample without filler, **R***

The coordination polymers (**PC-10** and **PC-11**) were used as fillers for PDMS, aiming to obtain composite materials with improved electromechanical or sensing properties. The mechanical properties of the materials were tested noting that the elongation at break, strain and Young's modulus increased with increasing the amount of complex incorporated into the siloxane matrix (Figure 67), indicating its reinforcing effect (MC-1: 5%, MC-2:10%, MC-3:20 % **PC-10** filler).

For the composite material containing 5% filler (MC-1), absorbance UV-Vis spectra were recorded. The analysis revealed the presence of three absorption bands in the 530-730 nm region. Considering the structure of the filler, in which the metal centers have different surroundings, it was decided to study the effect of solvent vapors. It was observed that upon increasing the exposure time, the absorption band from 612 nm undergoes a bathochromic shift to 630 nm, the compound changing its color from blue-green to intense blue, and the spectrum shows a hyperchromic effect, all absorption bands (586, 630 and 690 nm) becoming more pronounced (Figure 69). To see if the acetone vapor absorption process is reversible, UV-Vis spectra were recorded for the material left at rest under normal conditions. The material was monitored for 80 minutes, and the analysis showed a general hypochromic effect due to desorption of solvent vapors. It was also observed that the desorption process is much slower compared to the absorption process. During the 80 minutes of monitoring, the analysis revealed that the absorption band at 630 nm undergoes a slight hypsochromic shift to 623 nm (Figure 70). *The results of the performed tests recommend this material as an active element in sensors for the detection of solvent vapors*.

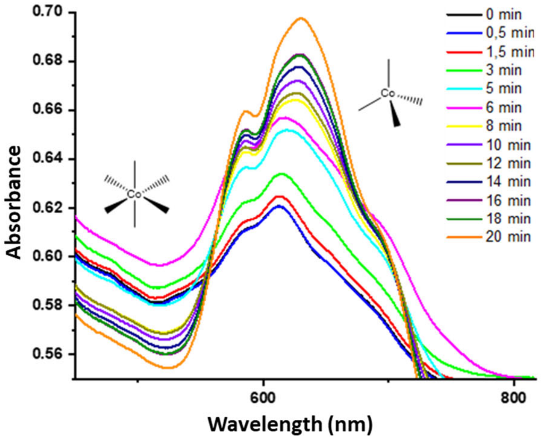


Figure 69. UV-Vis absorption spectra for composite MC-1, exposed to acetone vapors

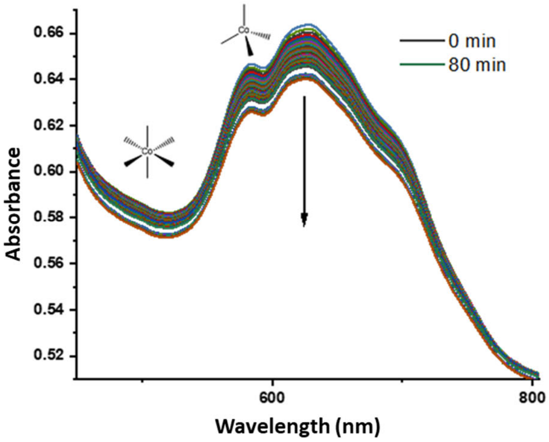


Figure 70. Change in time of the absorption spectrum in UV-Vis of the MC-1 composite after environmental exposureof acetone vapors

Another 2D coordination polymer used as a filler was **PC-11**. After delamination, the filler was incorporated into the matrix, in proportions of 1, 5 and 10 wt% (MC-4÷6). In all cases, a good compatibility with the silicone matrix was observed, since apparently homogeneous materials were obtained. Similar to **PC-10** based materials, the resulting materials are also cross-linked and stable in normal atmosphere.

The stress-strain curves (Figure 73) indicate that, at an amount of 1 and 5 wt% filler, the Young's modulus increases by about two times compared to the value recorded for the reference silicone sample, indicating a reinforcing effect of the filler, while the elongation at break decreases by 1.3-1.5 times. However, at 10 wt% filler loading, the pattern of the stress-strain curve and the values of tensile strength and Young's modulus approach those of the reference sample, while the elongation at break increases significantly, about 1.8 times compared to control sample, reaching 1664 %, which indicates the manifestation of other effects when increasing the filler amount.

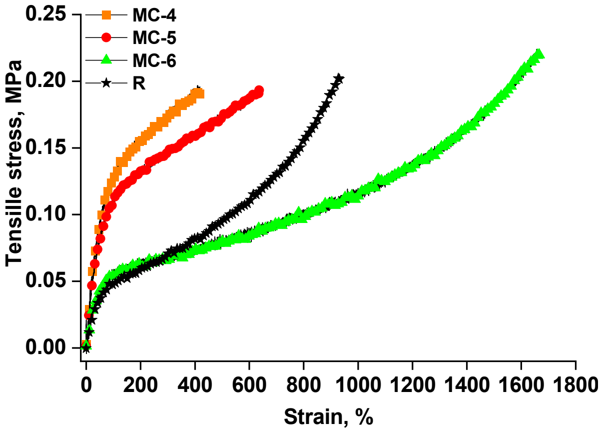


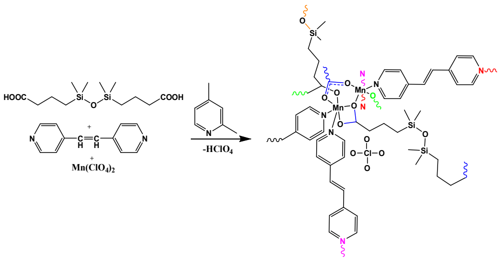
*Figure 73. Stress-strain curves for composites with **PC-11** filler and the reference material, **R***

III.2.2.2. Polymers or 3D Coordination Networks (PC 3D)

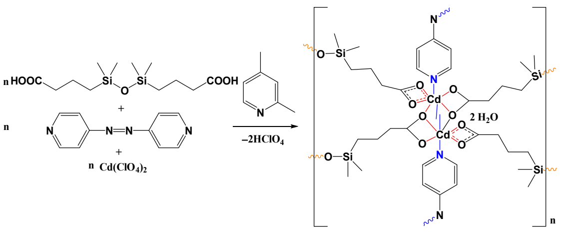
In recent decades, coordination polymers in the form of three-dimensional porous metal-organic frameworks (3D MOFs) which are generally characterized by substantial specific surface area, pronounced porosity and modifiable chemical structures have been extensively studied especially considering the possibilities for gas sorption and separation applications. Magnetic and electrical properties of flexible MOFs can be modulated by gas sorption [221,226]. MOFs exhibiting electrical conductivity have been studied for their potential uses in energy and sensor technologies. Unlike conventional MOFs, 3D coordination polymers are reported in this PhD thesis, which feature siloxane ligands, but the crystal structure of these coordination polymers is an extremely dense one, generally due to the high flexibility of the ligand. The obtained 3D polymers belong to the class of insulating materials, with good thermal stability.

III.2.2.2.1. Synthesis of 3D coordination polymers (3D PC)

In the attempts to synthesize 2D coordination polymers, by the technique that involves the use of a ligand and a co-ligand, with a slight change in the reactant ratio, two 3D coordination polymers were obtained (Schemes 24-25). The role of the co-ligand is to provide rigidity to the system, helping in the crystallization process.



Scheme 24. Synthesis reaction of the ***PC-13*** polymer



Scheme 25. Synthesis reaction of the ***PC-14*** polymer

III.2.2.2.2. Characterization of 3D coordination polymers

SC XRD analysis showed that **PC-13** is constituted by a 3D cationic coordination polymer and ClO_4^- anions. The asymmetric unit (Figure 77) comprises two Mn^{2+} ions in the general positions, 1.5 fragments of double deprotonated Cx^{2-} ligands, 2.5 ***etdipy*** molecules and a perchlorate counter-anion. The eight positive charges from four Mn(II) ions are counterbalanced by eight negative charges from three deprotonated Cx^{2-} ligands and two ClO_4^- anions outside the coordination sphere, so that the charge balance agrees with the formula $\{[Mn4(Cx)_3(etdipy)_5]\cdot 2ClO_4\}_n$.

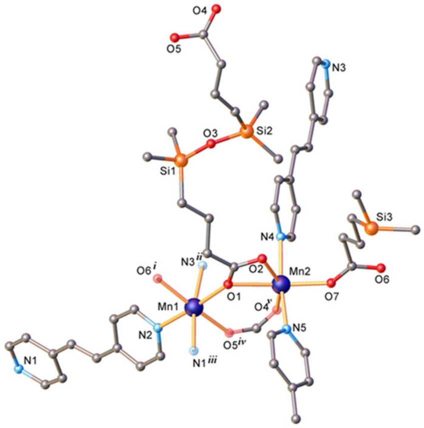


*Figure 77. The asymmetric unit, highlighting the coordination of the Mn(II) atoms in **PC-13**. ClO_4^- ions in the ionization sphere have been omitted for clarity. Atom positions generated by symmetry are shown in faded colors. Symmetry codes: $^{(i)}$ 1 – x, 1 – y, – z; $^{(ii)}$ x, ½ - y, ½ - z; $^{(iii)}$ – x, – ½ + y, ½ – z; $^{(iv)}$ – 1 + x, ½ – y, – ½ + z; $^{(v)}$ – 1 + x, ½ – y, – ½ + z.*

Both Mn(II) atoms have coordination number 6, but have different coordination geometries. The coordination polyhedron of Mn1 is described as a slightly distorted N_3O_3 octahedron. As for Mn2, if the three bridging carboxylate groups would have occupied a single coordination position, one could assume that the coordination geometry is a distorted trigonal bipyramid. The structure analysis revealed that the carboxylate groups perform three different functions, being coordinated as bidentate *syn-syn*, bidentate *syn-anti* and tridentate ligands, which generate the formation of the one-dimensional matrix, as shown in Figure 78. The distances Mn1···Mn2 and Mn1···$Mn2^{i}$ in the 1D coordination polymer are 5.72(15) Å and 3.85(13) Å, respectively. Further interconnection of the 1D chains occurs via the Cx^{2-} and ***etdipy*** linkers to form a dense three-dimensional coordination network, is shown in Figure 79.

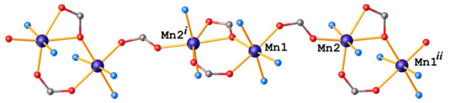


Figure 78. 1D arrangement of metal ions, highlighting the coordination functions of the carboxylate groups. Symmetry codes: (^{i}) x, ½ y, – ½ + z; (^{ii}) x, ½ – y, ½ + z

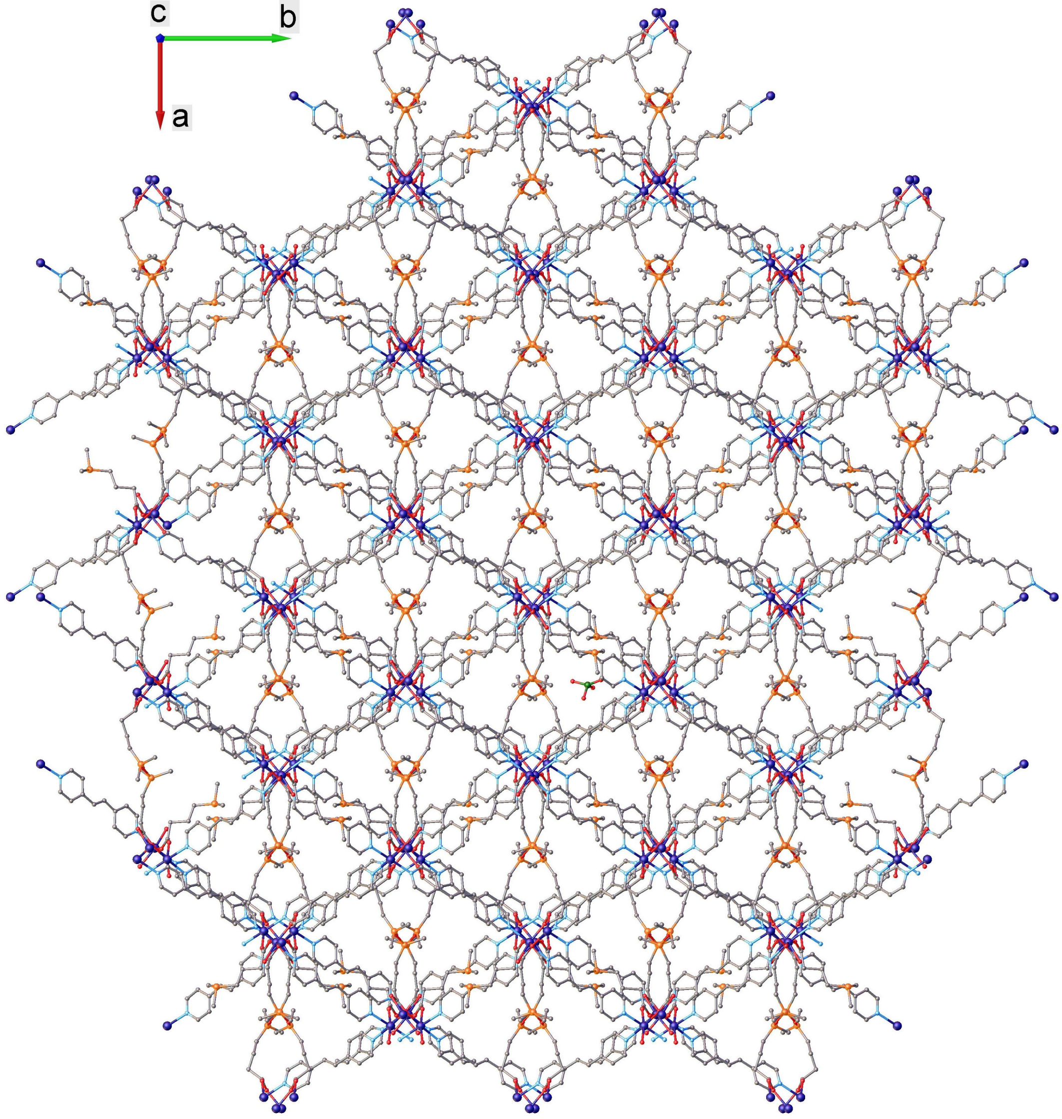


Figure 79. Crystal structure of compound ***PC-13***

The high density of the above-mentioned 3D network, as well as the presence of ClO_4^- counter-anions outside the coordination sphere and highly flexible, statistically disordered siloxane fragments, determine the drastic reduction of solvent accessible areas in the crystal. Using the functions in the Olex2 program, it was determined that the solvent accessible volume is less than 2.3%. The BET surface area estimated from nitrogen sorption isotherms is extremely low, of 0.478 m^2/g.

SC XRD analysis reveals (in the case of PC-14) the formation of an electrically neutral coordination polymer of the type $[Cd(CxAzoPy)\cdot 1.85H_2O]_n$ (the positive charges of the cadmium atom are counterbalanced by the negative charges of the doubly deprotonated ligand). The asymmetric unit is constituted by a double deprotonated ***H_2Cx*** molecule (Cx^{2-}), an ***AzoPy*** molecule and a Cd atom (Figure 87).

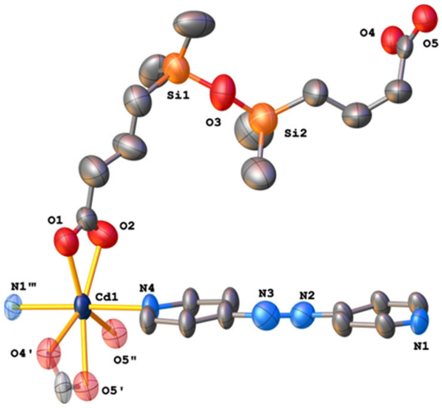


Figure 87. Asymmetric unit of compound ***PC-14****. Water molecules in the hydration sphere have been omitted for clarity. Atom positions generated by symmetry are shown in faded colors. Symmetry codes: ′) – ½ + x, ½ – y, – ½ + z; ″) 3/2 – x, ½ + y, 3/2 – z; ‴) – ½ + x, ½ + y, + z*

Two carboxylate groups in the disiloxane ligand show different structural functions being coordinated in k^2O,O' bidentate *syn-syn* and $k^3O,O':O$ tridentate-bridge modes. The Cd atom has coordination number 6, having an O_5N_2 surround in a bipyramidal-trigonal geometry, if each carboxylate group occupies a vertex of the coordination polyhedron. Also, there are dinuclear fragments in the 3D structure of the polymer, where the Cd-Cd interatomic distance is 3.84(11)Å.

It is noteworthy that the 3D lattice is stabilized by π-π interactions between the aromatic moieties, evidenced by the short centroid-centroid distance of 3.9(16) Å. A projection of the 3D polymer structure is illustrated in Figure S25, with the free solvent accessible volume being 896.8 Å^3 (14.8%), calculated using the Olex2 program.

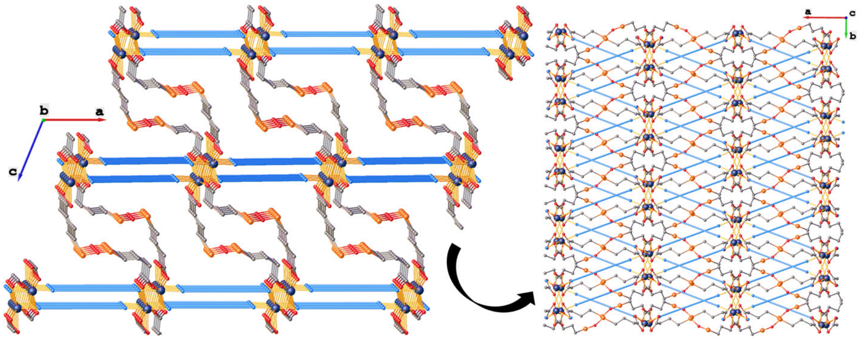


Figure S25 Polymer assembly mode following the ***H_2Cx*** *ligand. The* ***AzoPy*** *fragment has been replaced with a blue line for clarity*

The presence in the structure of ***AzoPy***, known for its ability of *trans-cis* photoisomerization [250], creates the prerequisites for the possibility of controlling some properties by UV-Vis irradiation. Literature studies highlight that the dielectric permittivity decreases through the photoisomerization of some coordination compounds of ***AzoPy***. This phenomenon was also observed in the case of the compound **PC-14**, but considering the three-dimensional structure of this compound, the photoisomerization phenomenon is reversible (Figure 94). The phenomenon was also captured in solution, following

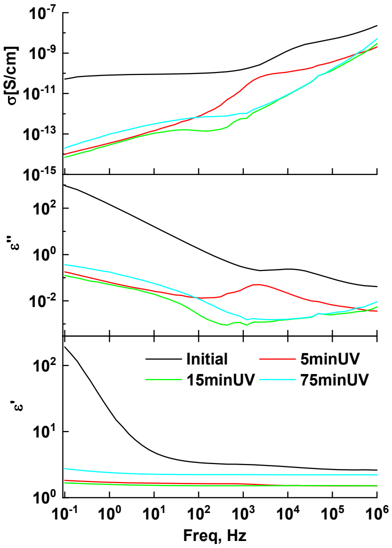


Figure 94. Dielectric spectrum for compound ***PC-14***

the changes in the UV-Vis spectra, at different irradiation times. A comparison of the spectra for **AzoPy** and **PC-14** is shown in Figure 91.

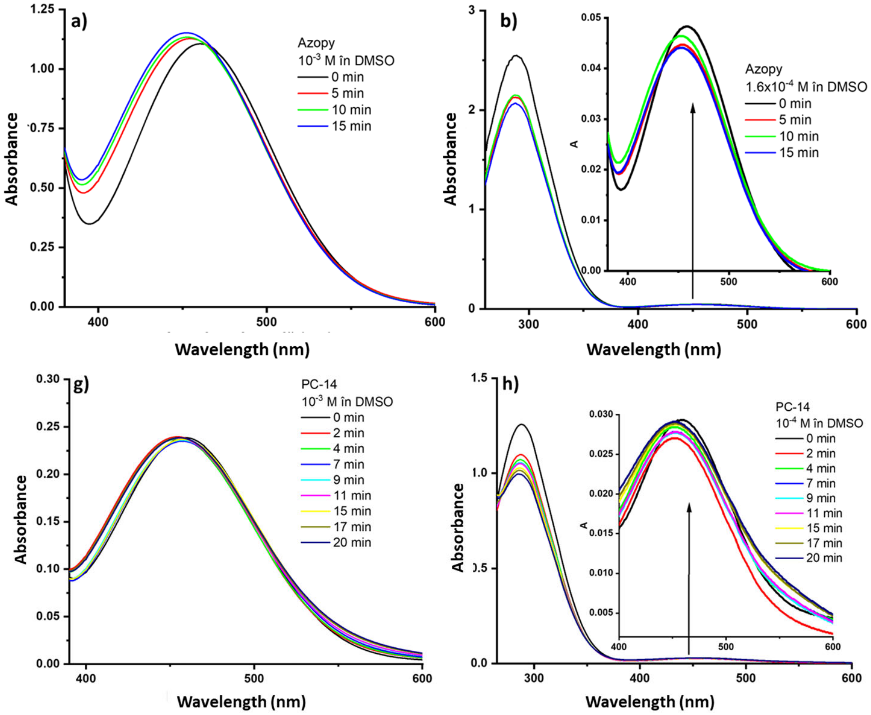


*Figure 91. The photoisomerization phenomenon revealed by the UV-Vis spectra of AzoPy and the **PC-14** compound in solutions of different concentrations (left - 10^{-3} M and right - 10^{-4} M)*

Both solution and solid-state studies highlight the reversibility of the system, thus strengthening the hypothesis that reversibility, even under continuous irradiation conditions, is due to the three-dimensional structure of the polymer.

III.2.2.2.3. The applicative potential of 3D coordination polymers

Taking into account the structure of the coordination polymers obtained, by which the premises of a good compatibility with the PDMS matrix are created, it was decided to introduce these complexes as fillers in such a matrix to obtain new composite materials, which can have combinations of interesting properties application. By adding fillers to the PDMS matrix, they can act as reinforcements, which can improve the mechanical properties of the composite material, and also influence the electrical or magnetic properties of the composite material, if this aspect is pursued.

Materials based on the 3D coordination polymer PC13 (MC-7÷MC-9)

The composite films based on **PC-13**, were tested to determine the mechanical properties. The analysis revealed that increasing the amount of filler takes to an increase of Young's modulus, thus indicating that the filler has a reinforcing role (Figure 97). The slight decrease in tensile strength with increasing filler amount could be due to the presence of crystalline agglomerates.

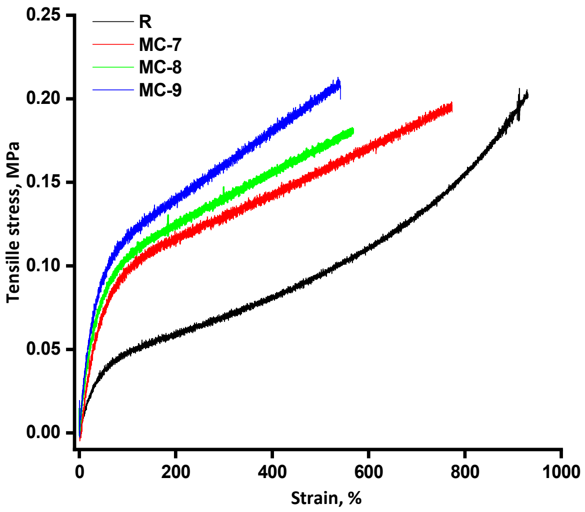


*Figure 97. Stress-strain curves for **PC-13** filler composites and reference material*

The dielectric strength increased with increasing filler amount. For the composite with 10 wt.% filler (MC-8) the value of the electric breakdown field has doubled, compared to the reference sample (Figure 98).

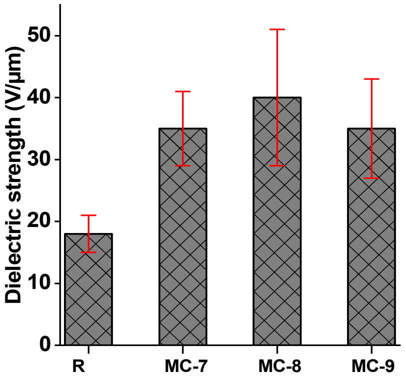


*Figure 98. Electric breakdown field values for **PC-13**-based materials*

Materials based on the 3D coordination polymer PC14 (MC10-MC11)

The investigation of composite materials from the point of view of mechanical properties was carried out by recording the stress-strain curves (Figure 101). The data obtained indicate that the introduction of the **PC-14** complex into the silicone matrix has a strengthening effect, leading to an increase in the Young's modulus values, but also in the strength and elongation at break, compared to the values recorded for the reference sample, *R*.

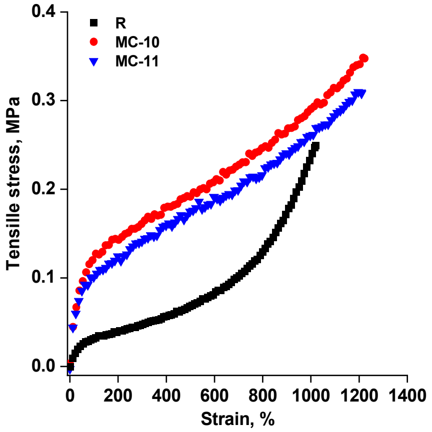


*Figure 101. Stress-strain curves of silicone composites with **PC-14**, compared to the reference sample*

Considering the dielectric properties of the filler and its behavior under UV irradiation, it was decided to investigate the properties of the composite materials, under the same conditions. For composites (Figure 102), the polarization phenomena at low frequencies are greatly diminished, so that the dielectric permittivity values are relatively small and constant over the entire frequency range studied. After five minutes of irradiation, changes in the dielectric constant of the composites can be observed compared to the reference. Variations of losses and conductivity with irradiation time are insignificant (in the range 0.1-10 Hz).

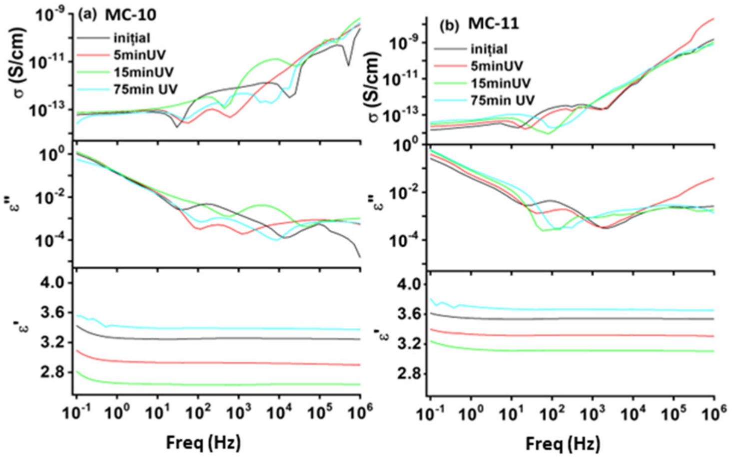


Figure 102. Dielectric spectra for the initial composites and after different irradiation times

The very low conductivity values indicate a strong insulating character of the **PC-14** complex. Continuing the irradiation (75 min.), the values of the dielectric parameters return to the initial ones or are even higher. These results follow roughly the same pattern of variation as those obtained in the case of UV-Vis irradiation of the **PC-14** compound in solution. One explanation could be that, under UV irradiation, isomerization initially occurs with the formation of a certain percentage of *cis* isomer. Due to the constraints imposed by the covalent 3D structure, the phenomenon is highly. The dielectric constants, higher than the initial ones, can be explained by the almost total formation of the trans isomer, assuming the existence of a small amount of the cis isomer in the initial sample is possible.

The influence of PC-14 complex amount in siloxane composites in the form of ~200 µm thick films on electrical breakdown resistance was investigated (Figure 103).

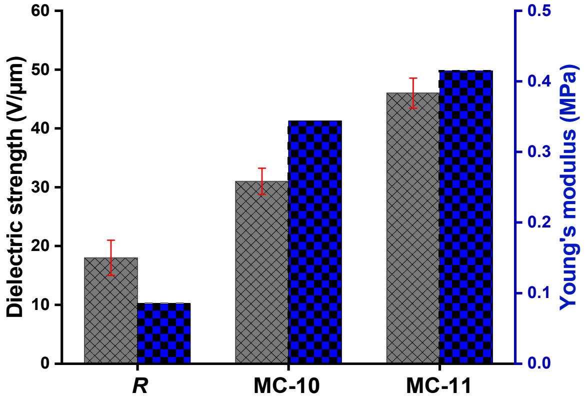


Figure 103. Dielectric strength and Young's modulus values of composites MC-10, MC-11, compared to the reference sample

The dielectric strength of the material increases with the increase of the filler addition, reaching, for a loading of 20% (sample MC-11), a value of 46 Vµm-1 which is more than double (155% increase) than that that of the reference (18 Vµm-1). This is due to the reduced energy dissipation, a fact reflected in the low dielectric loss values of the composites loaded with the coordination compound **PC-14**.

III.2.2.3. Coordination compounds with polycarboxylic ligands having an octakissilsesquioxane core

III.2.2.3.1. Polycarboxylated octakissilsesquioxanes proligands (COOH-PSx)

The CCDC database contains approximately 259 compounds based on T_8-POSS, in the form of organic compounds or complexes, some of which have been reported by our group. For **COOH-PS1**, crystals suitable for SC XRD analysis were obtained for the first time. The results of the SC XRD study for **COOH-PS1** are shown in Figure 105. The molecule $[HOOC(CH_2)_2S(CH_2)_2]_8Si_8O_{12}$ (**COOH-PS1**) occupies a special position on the inversion center, located in the center of the octasilsesquioxane cage.

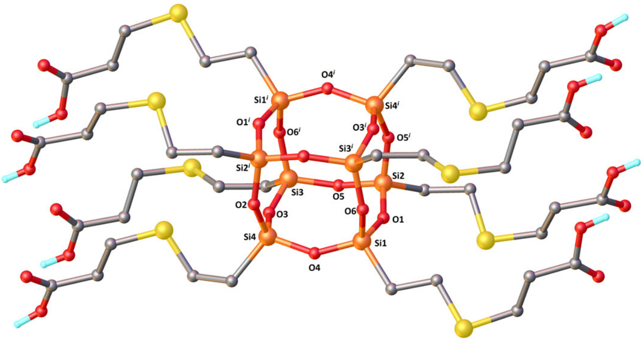


*Figure 105. X-ray molecular structure of $[HOOC(CH_2)_2S(CH_2)_2]_8Si_8O_{12}$ in the crystal structure of **COOH-PS1**. Irrelevant H atoms have been omitted for clarity*

The X-ray molecular structure of **COOH-PS1** demonstrates that the Si_8O_{12} fragment does not correspond to the ideal cubic arrangement, but adopts an elongated Si_8O_{12} cube configuration with eight carboxyethyl-thioethyl substituents, which is demonstrated by a comparison of the angles for Si1-O1-Si2=151.2(3)°, Si3-O3-Si4=151.5(4)° with Si1-O6-Si3′=147.5(4)°, Si2′-O5-Si4=148.7(3)° and interatomic distances Si1···Si2=3.129(5) Å, Si3···Si4=3.13(4) Å with Si1···Si3′ 3.1(4) Å, Si4···Si2′=3.095 (5) Å. The Si–C, Si–O, and C–S bond lengths fall within the narrow range of 1.827(7) ÷ 1.854(7) Å, 1.601(5) ÷ 1.629(5) Å, and 1.719(10) ÷ 1.812(9) Å, being consistent with values reported for other silsesquioxanes [258–260]. Although the Si-O-Si angle generally varies over a wide range, in this structure it approaches the tetrahedral angle and is quite similar to the perfect tetrahedral geometry. In the crystal, $[HOOC(CH_2)_2S(CH_2)_2]_8Si_8O_{12}$ entities form supramolecular chains, due to intermolecular O-H···O hydrogen bonds occurring between the carboxyl groups of adjacent molecules, as shown in Figure 106.

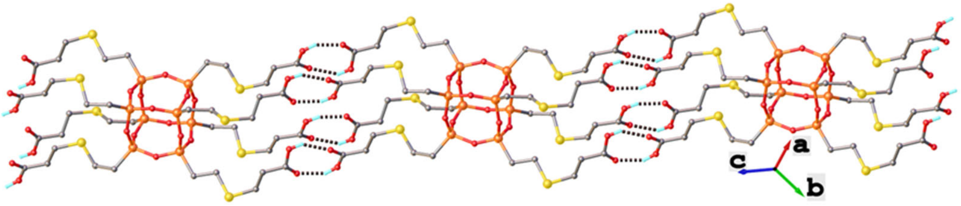


*Figure 106. Intermolecular hydrogen bonds in the crystal structure of **COOH-PS1***

The formation of COOH-PSx was confirmed by FTIR and ^{1}H-NMR spectroscopy. The asymmetric stretching vibration of Si-O-Si (υSi-O-Si) characteristic of the silsesquioxane cage appeared around 1112 cm^{-1} in **COOH-PS1** and 1117 cm^{-1} in **COOH-PS2**, indicating that the cage structure remained intact. FTIR spectra revealed the disappearance of absorption bands characteristic of the υC=C bond at 1607 and υC-H at 3069 cm^{-1} for the vinyl group, indicating that thiol-ene addition was complete. The absorption band characteristic of -COOH groups appeared at ~1710 cm^{-1}. In the ^{1}H-NMR spectra the complete disappearance of the signals from the vinyl groups ($-Si-CH=CH_2$) from 5.72–6.20 ppm and thiol (-SH) from 1.37 ppm of the reactants, coupled with the appearance of new signals in the aliphatic region ($-Si-CH_2-$ 1.06–1.07 ppm and $-CH_2-S-CH_2-$ 2.58–3.26 ppm) confirmed that the reaction is complete and thus the formation of silsequioxanes functionalized with thiopropionate or thioacetate. ^{1}H-NMR spectra of the compounds showed signals in intensity ratios matching the proposed structures. Similar to the hydrosilylation reaction, the thiol-ene addition reaction between alkenes and -SH leads to the formation of Markovnikov (α-) or anti-Markovnikov (β-) addition silsesquioxane derivatives [261]. In this case, only anti-Markovnikov (β-) products are present, probably due to steric hindrances generated by the silsesquioxane cage.

III.2.2.3.2. COOH-PSx coordination with metal ions

Silsesquioxanes functionalized with carboxyl groups (COOH-PSx), which differ in the length of the spacer ($(CH_2)_2-S-(CH_2)_2$ or $(CH_2)_2-S-CH_2$) between the carboxyl group and the silicon atom to which it is connected have been used as ligands for different metal(II) ions. To study the coordination ability of COOH-PSx, the carboxylic acid groups were deprotonated, resulting in sodium carboxylate salts, which should facilitate complexation [262]. COOH-PSx ligands were readily converted to COONa-PSx by treatment with sodium hydroxide in water at 25 °C, yielding amorphous precipitates. Coordination compounds with metals Cu^{2+}, Ni^{2+}, Cd^{2+} (COOM-PSx) were obtained but not as single crystals. They were analyzed by other complementary methods.

COOM-PSx were tested as catalysts for the decomposition of hydrogen peroxide (H_2O_2) in alkaline medium, according to a procedure described in reference [263], as well as for the photodecomposition of Congo red (CR). Both copper complexes were active catalysts for the former process and only **COOCu-PS2** showed good activity in the latter. No significant results were obtained for the rest of the complexes. Figure 107a shows the conversion as a function of time for **COOCu-PS1** and **COOCu-PS2** (calculated as the volume of O_2 formed relative to the theoretical volume, per gram of catalyst). **COOCu-PS2** was the most efficient catalyst for H_2O_2

decomposition, allowing a conversion of about 40% after 38 min, while in the presence of **COOCu-PS1** it was only 26% under the same conditions. This being a first-order reaction, plotting ln(C/C0) versus time (where C is the concentration of H_2O_2 – determined from the volume of O_2 and C0 is the initial concentration) gave the rate constants (k, s^{-1}) as the slope of the linear trendlines obtained for the first 1000 s (Figure 107b).

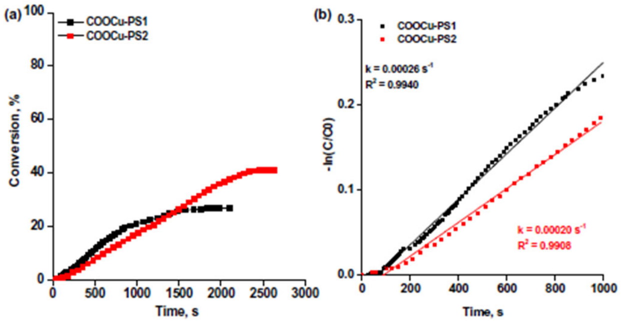


Figure 107. Evolution (a) and kinetics (b) of H_2O_2 decomposition in alkaline medium using ***COOCu-PS1/PS2*** *as catalysts*

COOCu-PS2 demonstrated increased catalytic activity for the photodegradation of CR under UV irradiation (Figure 108) without the addition of oxidizing agents or pH change. Based on the existing data, the catalytic activity is based on both the high hydrophilicity and the pore size, which allow the CR molecules to penetrate more rapidly into the active sites of the catalyst.

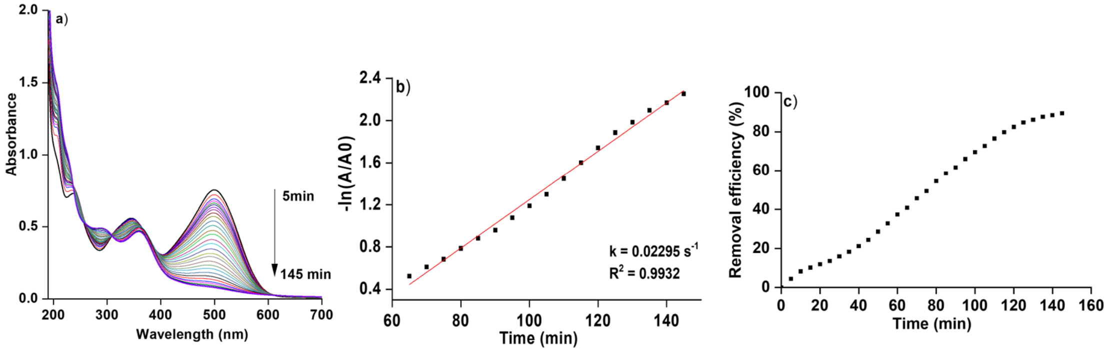


Figure 108. a) Evolution of the UV–Vis spectra of the Congo Red solution over time, in the presence of ***COOCu-PS2*** *as heterogeneous catalysts; b) graph − ln(A/A0) vs. time used to calculate the first-order reaction rate constant; c) degradation yield*

GENERAL CONCLUSIONS

In this thesis, 1,3-bis(2-aminoethylaminomethyl)tetramethyldisiloxane (SFA) was used as ligand precursor for Schiff bases, 1,3-bis(carboxypropyl)tetramethyldisiloxane and 1,3-bis(cyanopropyl)tetramethyldisiloxane as ligands, all bidentate and sharing the bis(methylidene)tetramethyldisiloxane structural motif as a very flexible and hydrophobic spacer. Based on them, coordination compounds of different dimensions, from 0D to 3D, were obtained, which were characterized from a structural point of view and for specific properties.. In the particular context, which appeared in metal complexation experiments with Schiff bases derived from SFA, theoretical calculations were successfully used to explain the reaction mechanisms. The compounds obtained show a series of interesting characteristics and potential use in various applications, thus attracting the attention of the scientific community.

The original contributions include:

●Experiments, supported by theoretical calculations, indicate that the siloxane bond undergoes hybridization processes that are influenced by the electron-donating atoms, from the β position to the silicon atoms, and by the experimental conditions, which leads to the fragmentation of the molecule with the formation of a mixture of compounds. The understanding of hybridization processes is essential to control and design compounds with specific properties. As a result of the experiments using 1,3-bis(2-aminoethylaminomethyl)-tetramethyldisiloxane (SFA) as a model, ten new structures were obtained, which were registered in the *CCDC* database. Based on theoretical and experimental data, a reaction mechanism was proposed to explain the behavior of this compound.

●The reaction between SFA and 3-formylsalicylic acid (3-FSA), and subsequent treatment of the mixture with copper salt, led to an original tetranuclear 0D complex, primarily through the presence of reactive silanol-type arms formed as a result of bond cleavage siloxanes. Unlike the coordination compounds of Schiff bases derived from 3-FSA with organic amines reported in the literature, in which the imine nitrogen atoms and the carboxylic oxygen are in the *cis* position, in the complex formed in the present case they are in the *trans* position, as the case of complexes of Schiff base derivatives with monoamines. This aspect would indicate that the breaking of the siloxane bond occurred prior complexation ending, a hypothesis confirmed by FTIR spectrometry. The highly reactive free silanol arms allow covalent attachment of the complex to suitable solid substrates, glass in this case. The presence of the complex on the glass surface was evidenced by AFM and MFM images. The latter show a high phase contrast, indicating the existence of magnetic properties, as would be expected for a tetranuclear copper derivative. XPS analysis demonstrated the chemical binding of the complex to the glass surface through the Si-O-Si bond. The possibility of immobilization on a solid, insoluble substrate creates the prerequisites for a very efficient utilization of the compound in applications such as single-layer detection or heterogeneous catalysis.

●Six 1D coordination polymers based on 1,3-bis(3-cyanopropyl)tetramethyldisiloxane and metal perchlorates were synthesized. Two 1D polymers were synthesized by the perchlorate counterion exchange reaction with iodide. The SC XRD analysis revealed that with the change of the counterion, there is also a change in the supramolecular architecture of the polymer. A 1D coordination polymer with *paddle wheel* building units based on copper benzoate and 1,3-bis(3-cyanopropyl)tetramethyldisiloxane was also obtained. DVS analysis revealed that the obtained polymers are hydrophilic. Moreover, they absorb atmospheric water until dissolution, this being a characteristic found in crystal hydrates (for example sodium or calcium chloride).

●Three 2D-type coordination polymers were obtained, two of which by the reaction between 1,3-bis(3-cyanopropyl)-tetramethyldisiloxane and cobalt thiocyanate or copper triiodide, respectively, while a third 2D coordination polymer was isolated as a secondary reaction product in the complexation reaction of cadmium with a mixture of ligands (1,3-bis(carboxypropyl)tetramethyldisiloxane and 4,4′-azopyridine). 2D PCs were analyzed by SC XRD, powder XRD and spectral analyses. The analyzes revealed the formation of some original compounds, the tetramethyldisiloxane fragments being located on the surfaces of the 2D layers, thus conferring hydrophobicity on the compounds, an aspect highlighted by the crystallographic analysis and confirmed by the DVS analysis. As a result, the interactions between the layers are weak, as Van der Waals forces.

●2D PCs can be an alternative to the already established 2D materials of an inorganic nature, offering the advantage of wide possibilities for fine control of the structure and implicitly of the properties, due to their modular character (organic and inorganic blocks). Although less explored from this perspective, they have the potential to address some of the requirements not covered by their inorganic counterparts. Among their main disadvantages, for which solutions are sought, are the stronger intermolecular interactions that cause their stacking and the low stability in humidity. The 2D coordination polymers developed here are original due to the presence on the surface of the nanosheet of methyl groups able to limit intermolecular interactions, allowing an easier delamination of the aggregates that are stacked during the formation and crystallization process and giving them hydrophobicity. The coexistence of polar (coordination blocks) and nonpolar (tetramethyldisiloxane spacers) building units gives these 2D PCs a certain surface activity and self-assembly capability in solution when they are soluble.

- Composite materials (MC-10, MC-11) based on PDMS and **PC-14**, have the ability to respond to stimuli (structuring by UV irradiation). For easier manipulation of these nanostructures in certain practical applications, they have the advantage of being more efficiently incorporated into polymer matrices and thin films compared to 3D MOFs. The hydrophobic character of the surface of the nanosheets gives them compatibility with hydrophobic matrices, a first choice being polydimethylsiloxanes.

- Two three-dimensional coordination polymers of the 3D MOF type were obtained. The reaction of 1,3-bis(carboxypropyl)tetramethyldisiloxane, 1,2-di(4-pyridyl)ethylene and $Mn(ClO_4)_2$ in the presence of 2,4-lutidine gave the first 3D MOF containing a flexible siloxane moiety reported by our group. SC XRD analysis revealed that the coordination polymer has a dense 3D network structure, as confirmed by BET analysis. The hydrophobic character of the studied compound was highlighted by the low water vapor sorption capacity, and by maintaining the integrity of the water drop rolled on the surface of the compound. The polymer demonstrated stability in an inert atmosphere up to 300 °C, with a glass transition at 24 °C. The compound is an electrical insulator and due to its hydrophobicity, this characteristic is not affected by environmental humidity. The magnetic results indicated a dominant antiferromagnetic interaction along the chain in the polymer, highlighting the presence of two types of chain bridging. An original 3D coordination polymer was also obtained by coordinating cadmium from $Cd(ClO_4)_2$ with mixed ligands consisting of 1,3-bis(3carboxypropyl)tetramethyldisiloxane and 4,4′-azopyridine. The structure was determined by elemental, spectral, and SC XRD analysis, with analyzes indicating extremely close packing and, as a result, very low porosity (14.8% low free volume) and high hydrophobicity (2.7% water sorption at RH 90%) conferred by the high flexibility and hydrophobicity of the tetramethyldisiloxane spacer. The compound does not exhibit the expected fluorescence based on the presence of cadmium in the structure, and the trans-cis isomerization of the azopyridine in the structure is limited by the dense packing and highly flexible ligand. Instead, it has been shown to be a good mechanical and dielectric reinforcement for a silicone elastomer when incorporated as a filler. The high dielectric strength is of interest for the application of the resulting elastomeric composites in electromechanical transducers. Theoretical calculations based on mechanical and dielectric parameters suggest that these silicon composites are suitable for electromechanical transducers operating in generator mode.

Synthesis of new coordination compounds

Within the thesis, 25 new fully characterized structures are reported, part of them being registered in the *CCDC* crystallographic database, of which:

- Nine 0D structures with fully organic ligands;
- An 0D structure (a tetranuclear copper complex) with a free silanol function;
- Nine 1D PC based on 1,3-bis(3-cyanopropyl)tetramethyldisiloxane and various metal salts;
- Two 2D-type PCs based on 1,3-bis(3-cyanopropyl)tetramethyldisiloxane and cobalt thiocyanate or copper triiodide, respectively;
- A 2D-type PC based on 1,3-bis(carboxypropyl)tetramethyldisiloxane, azopyridine, and cadmium perchlorate, isolated as a reaction byproduct;
- Two 3D PCs based on 1,3-bis(carboxypropyl)tetramethyldisiloxane and 1,2-di(4-pyridyl)ethylene with $Mn(ClO_4)_2$ and 4,4′-azopyridine with $Cd(ClO_4)_2$, respectively;
- A new ligand, octakis(2-carboxypropyl-thioethyl)silsesquioxane.

Also, one ligand in the form of oil and eight coordination compounds in the form of amorphous powders were obtained, their structure being demonstrated by complementary techniques.

Properties studied depending on the type of compound/material

- chemical reactivity and reaction mechanism of SFA;
- water vapor sorption capacity;
- thermal stability;
- mechanical properties;
- dielectric properties;
- response to stimuli (solvent vapors, UV-Vis light);
- magnetic properties.

Materials developed based on the obtained compounds:

- glass functionalized with the coordination compound 0D;
- PC 2D-silicone composites;
- PC 3D-silicone composites.

Potential applications identified:

- sensors (optical, magnetic, electromechanical);
- electromechanical actuators;
- electromechanical generators.

The results of the thesis reveal the significant potential that coordination compounds based on bidentate ligands containing the tetramethyldisiloxane spacer have for the development of new functional materials and technological applications. However, there are still many aspects to be researched and optimized to fully explore the potential of these compounds, thus opening up new research directions that can make valuable contributions to the field of chemistry and advanced materials.

PERSPECTIVES

The accumulated experience and the results obtained as well as the challenges that arose during the elaboration of the thesis constitute the motivation for continuing research in some directions as:

- Design and optimization of syntheses to obtain structures with desired dimensionality and expand the range of coordination structures, including by using new ligands to develop a diverse library of compounds with functional potential in different fields;
- The advanced characterization of these compounds to value their possible optical, magnetic, catalytic properties, etc.;
- Continuing research to identify and develop advanced practical applications of these compounds, such as optical, magnetic and electromechanical sensors, catalysts, controlled drug delivery systems, energy storage materials, in pollution control and environmental protection, etc.

Scientific activity and dissemination

The original results presented in the thesis were published as scientific articles in ISI-listed international and national journals.

Papers published in ISI journals

1. **Stoica A.-C.**, Damoc M., Tiron V., Dascalu M., Coroaba A., Shova S., Cazacu M. Silanol-functionalized tetranuclear copper complex and its nanoscale-heterogenization by immobilization on glass surface from solution. Journal of Molecular Liquids, 344, 117742 (2021). https://doi.org/10.1016/j.molliq.2021.117742 (**IF = 6.0**)

2. **Stoica A.-C.**, Damoc M., Zaltariov M.-F., Racles C., Cazacu M. Two-dimensional coordination polymers containing permethylated motifs - promising candidates for 2D emerging materials. Structural, behavioral and functional particularities. Reactive and

Functional Polymers, 168, 105039 (2021). https://doi.org/10.1016/j.reactfunctpolym.2021.105039, (**IF = 5.1**)

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Papers published in ISI rated journals (results are not included in the thesis)

1. Dămoc M., **Stoica A.C.,** Macsim A.M., Dascălu M., Zaltariov M.F., Cazacu M. Salen-type Schiff bases spaced by the highly flexible and hydrophobic tetramethyldisiloxane motif. Some synthetic, structural and behavioral particularities. Journal of Molecular Liquids, 316 113852, (2020). https://doi.org/10.1016/j.molliq.2020.113852 (**IF = 6.0**)
2. Damoc M., **Stoica A.-C.,** Dascalu M., Asandulesa M., Shova S., Cazacu M. Dual crystalline–amorphous salen–metal complexes behave like nematic droplets with AIEgens vistas. Dalton Transactions, 50, 13841-13858, (2021). https://doi.org/10.1039/d1dt01980e (**IF=4.0**)
3. **Stoica A.-C.**, Damoc M., Baltag L., Macsim A.-M., Nicolescu A., Dinu M.V., Ionita G., Cazacu M. One-pot reduction-hydrophobization of heterogenized platinum with 1,1,3,3-

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4. Damoc M., **Stoica A.-C.,** Blaj D., Macsim A.-M., Dascalu M., Cojocaru C., Shova S., Cazacu M. Fourteen-member silacycle built by cascade reactions induced by a platinum catalyst. Journal of Molecular Structure. 1269, 133760 (2022). https://doi.org/10.1016/j.molstruc.2022.133760 (**IF = 3.8**)

5. Damoc M., Tigoianu R. I., **Stoica A.-C.,** Macsim A.-M., Dascalu M., Shova S., Cazacu M. Micellization turned on dual fluorescence and room temperature phosphorescence by pseudo-ESIPT in thiadiazole derivatives. Journal of Physical Chemistry C, 127, 99-109 (2022). https://doi.org/10.1021/acs.jpcc.2c07651 (**IF = 3.7**)

Patent application

1. Racleș C., Cazacu M., **Stoica A.-C.,** Diac C Process for reuse of exhausted catalytic converters, A/00272/2020

2. Bele A., Cazacu M., **Stoica A.-C.**, Racleș C., Tiron V., Burducea I., Process for obtaining a module of polymeric pressure sensors for detecting a mechanical impact, A/00664/2023

Research projects with national funding

1. Eco-innovative technologies for recovering of the platinum group metals from scrap catalytic convertors- ECOTECH-GMP, PN-III-P1-1.2-PCCDI-2017-0185.
2. Emerging 2D materials based on two-dimensional permethylated metal-organic networks, PN-III-P4-ID-PCE-2020-2000.

Research internships

1. Institute of Organic Synthesis at Taras Shevchenko National University of Ukraine, Kiev, 28.08-27.10.2021, Project- H2020-MSCA-RISE-2016, SPINSWITCH No. 734322.
2. Rigaku, MINIFLEX TRAINING (EUROPE), Neu-Isenburg, Germania, 09-10 October 2023.

Participation in thematic schools

1. The international school on innovations in homogeneous and supported homogeneous catalysis, 25-28.04.2023, București, România.
2. Thematic school vibrational and electronic spectroscopies applied to the study of reaction mechanisms - MECAREACT, 18-23.06.2023, Paris, France

Awards

1. ***Gold medal*** *for the poster*: Racleș C., Cazacu M., **Stoica A.-C.,** Diac C. Process for reuse of exhausted catalytic converters. XXIVth International Exhibition of Inventics, 29-31.07.2020, Iași, România

2. ***Best Young Scientist Poster Presentation*** for poster: Stoica A.-C., Dascalu M., Damoc M., Cazacu M. Some coordination polymers with pyridine-based ligands: synthesis and structural characterization. Progress in Organic and Macromolecular Compounds, 29th Edition, 4-6.10.2023, Iasi, Romania.

Communication

1. **Stoica A.-C.**, Dămoc M., Cazacu M. O abordare originală asupra unui nou catalizator eterogen pe bază de Pt(0), Scientific Communications Of Young Researchers MacroYouth'2020, 1st Edition, Iasi, November 19, 2020

2. **Stoica A.-C.**, Damoc M., Stiubianu G., Cazacu M. Permethylated two-dimensional metal-organic frameworks - promising candidates for emerging 2D Materials. AAAFM-UCLA International Conference on Advances in Functional Materials, 18.08.2021, California, Los Angeles.

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6. Damoc M., **Stoica A.-C.**, Dascalu M., Macsim A.-M., Tigoianu R.I., Blaj D., Rusu A.G., Iacob M., Cazacu M. Siloxane/silane derivates based on 5-amino-1,3,4-thidiazole-2-thiol and their gold complexes: interfacial phenomena based on photoluminescence. A XXVIII-a Sesiune de Comunicări Științifice a Institutului de Chimie Macromoleculară „Petru Poni" Iași Progrese în Știința Compușilor Organici și Macromoleculari, 7-9.10.2021, Iași, România

7. Damoc M., Tiron V., Tugui C., Varganici C.-D., **Stoica A.-C.**, Novitchi G., Dascalu M., Cazacu M. A Ferronematic Co(II) coordination compound suitable as active filler for

magnetically actuated materials. A XXVIII-a Sesiune de Comunicări Științifice a Institutului de Chimie Macromoleculară „Petru Poni” Iași Progrese în Știința Compușilor Organici și Macromoleculari, 7-9.10.2021, Iași, România

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12. **Stoica A.-C.**, Dămoc M., Dascălu M., Cazacu M. Tetranuclear complex of 3-formylsalicylic acid schiff base carrying silanol tails, 21st Romanian International Conference on Chemistry and Chemical Engineering, 4-7 septembrie 2019, Constanța - Mamaia, România

13. Dămoc M., **Stoica A.-C.**, Dascălu M., Iurașcu A.-M., Cazacu M. Salen-type ligands derived from a highly flexible organic-inorganic diamine and their metal complexes, 21st Romanian International Conference on Chemistry and Chemical Engineering, 4-7 septembrie 2019, Constanța - Mamaia, România

14. **Stoica A.-C.**, Damoc M., Dascalu M., Cazacu M. Liganzi și complecși metalici pe bază de 1,3-bis(2-aminoetilaminometil)tetrametildisiloxan, , A XXVII-a Sesiune de Comunicări Științifice a Institutului de Chimie Macromoleculară „Petru Poni” Iași Progrese În Știința Compușilor Organici Și Macromoleculari, 2-4 octombrie 2019, Iași, România

15. Dămoc M., **Stoica A.-C.**, Dascălu M., Iurașcu A.-M., Cazacu M. Baze Schiff de tip salen ale 1,3-bis(3-aminopropil)-tetrametildisiloxanului și complecși metalici ai acestora, , A XXVII-a Sesiune de Comunicări Științifice a Institutului de Chimie Macromoleculară „Petru Poni” Iași Progrese În Știința Compușilor Organici Și Macromoleculari, 2-4 octombrie 2019, Iași, România

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1. **Stoica A.-C.**, Dascalu M., Damoc M., Cazacu M. Some coordination polymers with pyridine-based ligands: synthesis and structural characterization. Progress in Organic and Macromolecular Compounds, 29th Edition, 4-6.10.2023, Iasi, Romania.

2. Damoc M., **Stoica A.-C.**, Cazacu M. Engineering organic heterocycles and silacycles through a Pt(II) catalyst. The international school on innovations in homogeneous and supported homogeneous catalysis, 25-28.04.2023, București, România.

3. Damoc M., Tigoianu R.I., **Stoica A.-C.**, Cazacu M. High-energy intermolecular proton transfer generating multiple emissions in aminothiadiazole derivatives. Thematic School Vibrational and Electronic spectroscopies applied to the study of reaction mechanisms – MECAREACT, 18-23.06.2023, Paris, France

4. Dascalu M., **Stoica A.-C.**, Bele A., Yu L., Ionita D., Vasiliu A.-L., Skov A.L., Racles C., Cazacu M. An approach to develop silicone elastomers with enhanced electromechanical transduction properties based on multicarboxy-POSS. 10th European Silicon Days, 10-12.07.2023, Montpellier France.

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9. **Stoica A.-C.**, Zaltariov M.-F. Antioxidant activity and biosynthetic process of spirulina platensis of a new ferrocenyl schiff base, 9th International EuroAliment Symposium, 5-6 septembrie 2019, Galați, România

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11. **Stoica A.-C.**, Vlad A., Dascălu M., Dămoc M., Tiron V., Cazacu M. Polimer de coordinare 2D al Mn(II) capabil să se autoasambleze și să răspundă la un stimul magnetic, A XXVII-a Sesiune de Comunicări Științifice a Institutului de Chimie Macromoleculară „Petru Poni” Iași Progrese În Știința Compușilor Organici Și Macromoleculari, 2-4 octombrie 2019, Iași, România

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