UNIVERSITY OF BUCHAREST
FACULTY OF CHEMISTRY
DOCTORAL SCHOOL IN CHEMISTRY

PhD THESIS

ABSTRACT

HOMOMETALLIC AND HETEROMETALLIC COORDINATION COMPOUNDS OBTAINED FROM SCHIFF-MANNICH BASE LIGANDS

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2023

Table of content (according to the PhD thesis)

ORIGINAL CONTRIBUTIONS

Introduction

Over time, coordination chemistry experienced a real development through the identification, classification and understanding of the formation processes of coordination compounds. One of the important pillars of coordination chemistry is the ligand that can allow the generation of coordination complexes with particular structural aspect and desired properties. From this category of ligands, Schiff bases and Mannich bases are often used due to their relatively easy synthesis, varied denticity and sites that have the ability to selectively interact with metal ions of a certain stereochemical preference. At the same time, the reduction and oxidation of the metal ion or the substitution of the ligand are reactions that can induce changes in the chemical and physical properties of the compounds. Unlike Schiff bases, Mannich bases show greater flexibility due to the lack of a C=N double bond making the accommodation of metal ions easier.

Transition metal complexes are noted not only because of their interesting properties and functionalities, but also because of the beauty of their crystal structure and the variety of colors that the crystals of the compounds present.

As a result of this variety and complexity in the synthesis of compounds, coordination chemistry represents an attraction with inexhaustible sources, but also with challenges, which is why in this work the compound of transition metals with bases Schiff, Mannich bases and ligands showing both arms, Schiff-Mannich were evaluated and investigated, from the structural point of view, but also their properties were studied.

Thus, the doctoral thesis with the title Homometallic and Heterometallic Coordination Compounds Obtained from Schiff-Mannich Bases aims to approach various strategies in the synthesis of coordination compounds, their characterization and the investigation of potential properties.

The doctoral thesis includes a theoretical part structured in two chapters (chapters I and II) and an original part (chapters III, IV, V and VI). The literature part of the paper is dedicated to the Mannich reaction by which ligands with varying denticities are generated and, also to the coordination compounds obtained using these ligands called Mannich bases (chapter I).

Chapter II of the literature part focuses on ligands that simultaneously present the Schiff arm and the Mannich arm highlighting their importance in the structural design of coordination complexes and on the potential properties of the final compounds. Coordination complexes selected from the literature for this chapter are structurally described, and magnetic or biological properties are presented. An important aspect in these chapters, besides highlighting the synthesis strategies, was the description of the principles of magneto-structural correlation, supported by examples from the literature.

Study directions in the original part:

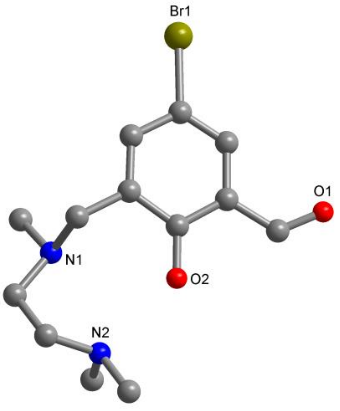
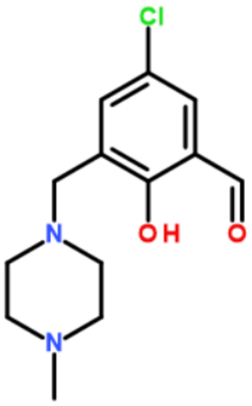
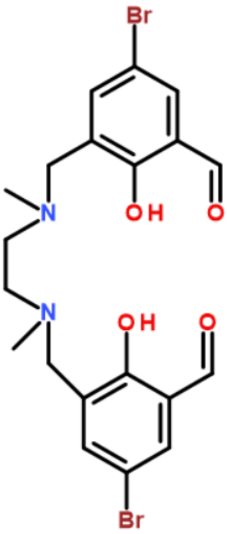
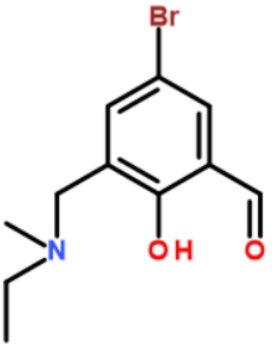
- Synthesis of Mannich bases starting from 4-chloro- or 4-bromo-salicylaldehyde and various secondary amines (N,N,N'-trimethyl-ethylenediamine, methyl-piperazine, N,N'-dimethyl-ethylenediamine, methyl-ethyl- amine);
- Self-assembly of Mannich bases with metal ions CoII, NiII, CuII;
- Synthesis of Schiff bases and the corresponding metalloligands starting from salicylaldehyde or o-vanillin and various (di)amines;
- Self-assembly of metalloligands with hexfluoroacetylacetonato derivatives of CoII, NiII, CuII;
- Synthesis of mixt ligands, Schiff-Mannich;
- Self-assembly of small ligands with metal ions CuII, NiII, CoII, ZnII;
- Synthesis of metallacyclophanes [Ni2Na2] and [Ni2K2];
- Structural and spectral characterization of the synthesized compounds;
- Performing magnetic studies, biological studies and performing DFT calculations.

Original contributions

In Chapter III of the doctoral thesis, the first two research directions mentioned above are addressed. Thus, the Mannich bases, HL^1 – HL^4 (Table 1) synthesized by the reaction of 4-chloro- or 4-bromo-salicylaldehyde with secondary amines (N,N,N'-trimethyl-ethylenediamine, methyl-piperazine, N,N'-dimethyl -ethylenediamine, methyl-ethyl-amine) were characterized by NMR spectrometry, and the structure of the Mannich base HL1 was also determined by single-crystal X-ray diffraction.

The coordination versatility of the four Mannich bases was highlighted by the use of CuII, NiII, CoII, ZnII salts (perchlorates, tetrafluoroborates, nitrates) or hexafluoroacetylacetonates, generating a series of 11 complex combinations: $[Cu(L^1)(hfac)]$ (**1**), $[Co_2(L^1)_2(hfac)_2]$ (**2**), $[Ni_2(L^1)_2(hfac)_2]$ (**3**), $[Ni_2(L^2)_2(NO_3)(H_2O)_2]\cdot(NO_3)(H_2O)$ (**4**), $[Ni_2(L^1)_2(NO_3)_2(4,4'\text{-bipy})]$ (**5**), $[Ni_2(L^1)_2(NCS)_2]$ (**6**), $[Co_2(L^1)_2(NCS)_2]$ (**7**), $[Cu_2(L^1)_2(NCS)_2]\cdot(H_2O)$ (**8**), $[Cu_2(L^1)_2]\cdot(ClO_4)(CH_3OH)$ (**9**), $[Ni_2(L^1)_2(CH_3CN)]\cdot(ClO_4)_2(CH_3CN)$ (**10**), $[Cu(H_2L^3)(H_2O)]\cdot(BF_4)_2(H_2O)$ (**11**).

Tabel 1. Structural representation of the Mannich bases synthesized and used in this thesis.

	
HL^1	**HL^2**
	
H$_2$L^3	**HL^4**

The synthesized compounds were characterized by single crystal X-ray diffraction and the FTIR and UV-Vis spectra were discussed. From the structures of the compounds, it can be observed that the anions of the raw materials (nitrate, hexafluoroacetylacetonate) or the sulfocyanide anion have the role of co-ligands. In the structure of compound 5 (Figure 1) it is observed that 4,4'-bipy functions as a bridge. In compound 6 (Figure 1), the sulfocyanide anion coordinates terminally while in compound 8 (Figure 1) it acts as a bridge. It should be noted that the structure of compound 10 (Figure 1) shows two nickel(II) ions in different stereochemistries (octahedral and square pyramidal - being rarely encountered in the coordination chemistry of nickel(II)).

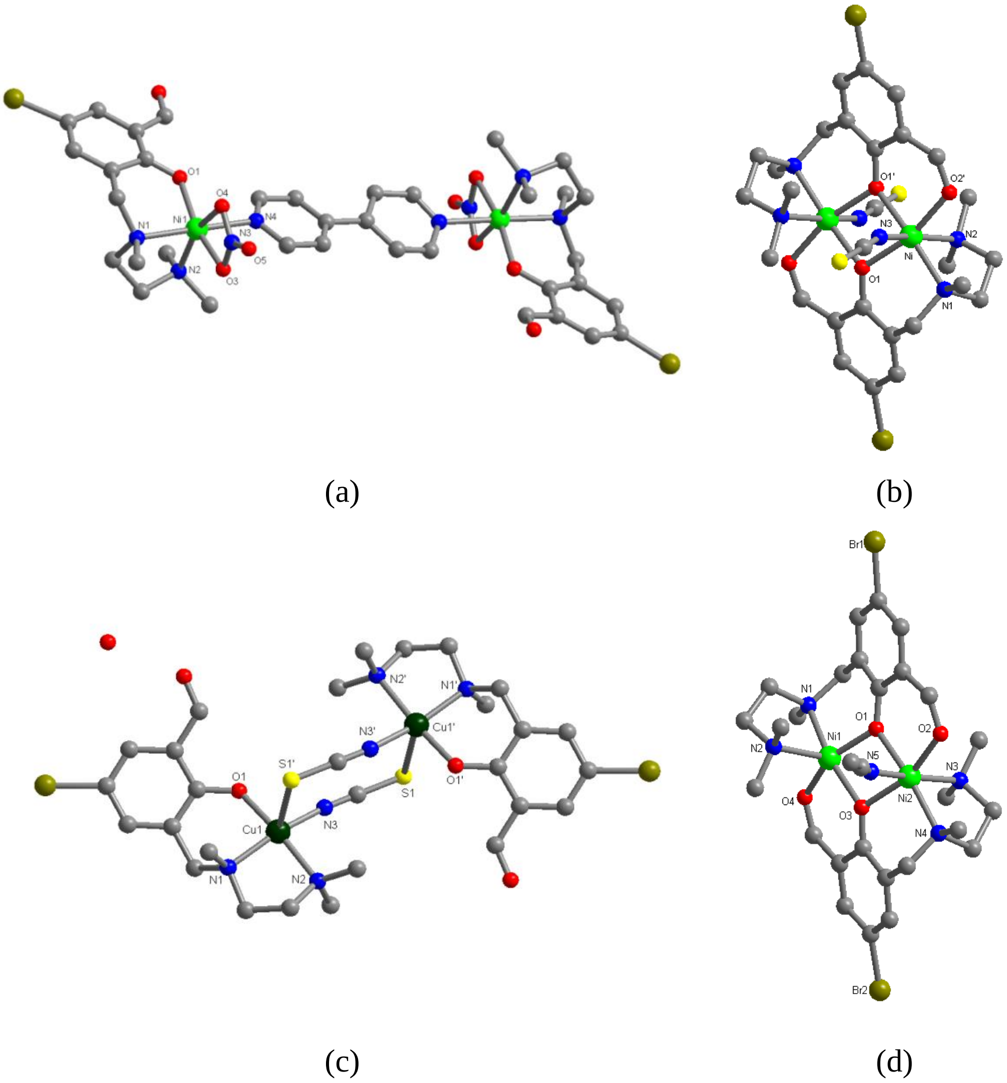
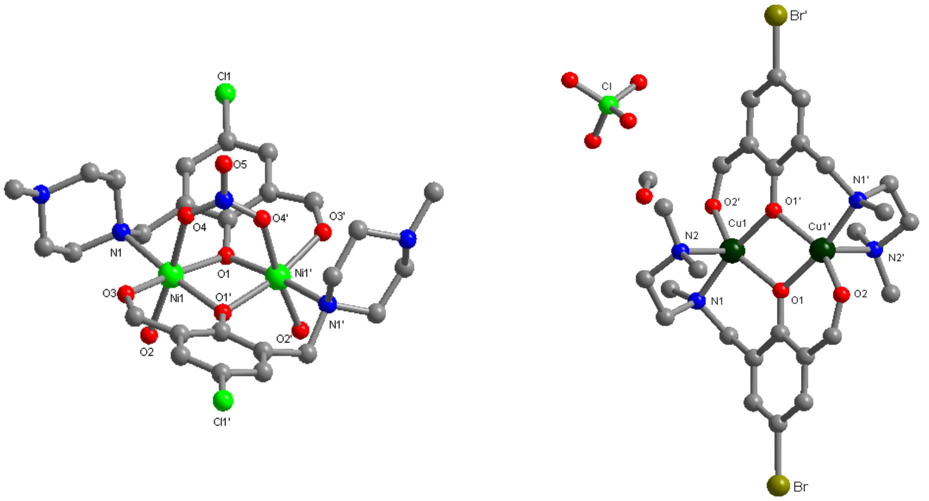


Figure 1. Structures of compounds (a) 5, (b) 6, (c) 8, and (d) 10. Hydrogen atoms have been omitted for clarity. Also, the uncoordinated water molecule in compound 8 , the uncoordinated perchlorate anions and the methanol molecule in compound 10 have been omitted for clarity of the structures.

It is known from the literature that Mannich bases and certain dinuclear complexes show biological activities (being used as study models), which is why it was desired to investigate the biological behavior for two of the compounds of this series. For compounds **4** and **9** (Figure 2) and the corresponding ligands, a biological, preclinical study was carried out, determining the in vitro cytotoxicity on HepG2 cells (human liver cancer cell line) by the XTT colorimetric test based on the transformation of the reagent 2,3- of bis-(2-methoxy-4-nitro-5-sulfophenyl)-2H-tetrazolium-5-carboxanilide (XTT) to formazan (orange color) by metabolically active cells in the presence of the reducing agent, phenazine metasulfate (PMS). The antioxidant capacity (in vitro) was also determined for the same compounds. A higher antioxidant activity was found for compound **9**.



(a) (b)

Figure 2. Structures of compounds (a) 4, symmetry code: ’ = -x, y, 0.5 -z and (b) 9, symmetry code: ’ = 2-x, -y, -z. Hydrogen atoms have been omitted for clarity.

It can be seen in Figure 3 that both compounds and ligands significantly reduce the viability of HepG2 cells in a dose-dependent manner ($p < 0.05$) compared to control cells. Compound 9 induces greater cytotoxicity against HepG2 cells at concentrations between 4.5×10-5 and 5×10-4 M, with cell viability being reduced to 20 and 90%, respectively (Table 2).

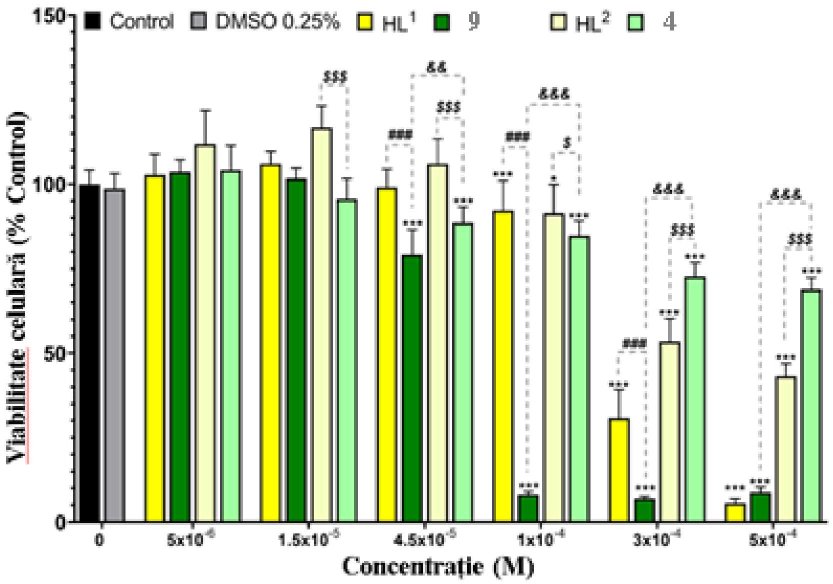


Figure 3. Cytotoxic effect of HL^1, **9**, HL^2 and **4** on HepG2 cells. The results are expressed as the mean ± SD of three identical experiments done in triplicate and analyzed using the independent t-student test. *$p<0.05$, ***$p<0.001$ in comparison with the Control sample; ###$p<0.001$ versus HL1; \$$p < 0.05$, \$\$\$$p < 0.001$ vs. HL2;&&$p < 0.01$, &&&$p<0.001$ vs. **4**. SD = standard deviation.

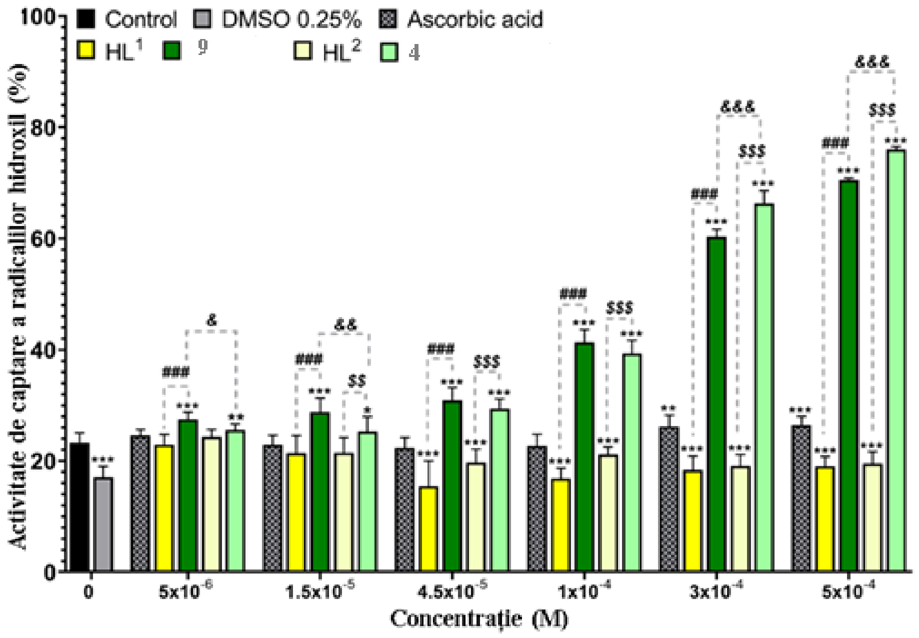


Figure 4. The antioxidant effect of ascorbic acid, HL^1, **9**, HL^2 and **4** expressed in percentage of hydroxyl radical scavenging activity of the compounds at different concentrations (5x10-6 - 5x10-4 M). Results are expressed as mean ± SD of five identical experiments, done in duplicate and analyzed using independent student t-test.*p < 0.05, **p < 0.01, ***p < 0.001 compared to Control; ###p < 0.001 vs. HL1; $$p < 0.01, $$$p < 0.001 vs. HL2; &p < 0.05, &&p < 0.01, &&&p < 0.001 compared to compound **4**.

Table 2. IC$_{50}$ (M) value of the compounds.

Compounds	IC$_{50}$ ± SD (M)
HL^1	$2,67x10^{-4} \pm 0,25x10^{-4}$
9	$6,35x10^{-5} \pm 0,49x10^{-5}$ ***, $$$
HL^2	$4,03x10^{-4} \pm 0,32x10^{-4}$ ***
4	$7,56x10^{-4} \pm 1,11x10^{-4}$ ###

Results are expressed as mean ± SD and analyzed using Student's independent t-test; *** p<0.001 vs. HL1; ###p<0.001 vs. HL2; $$$p<0.001 vs. compound 4, SD = standard deviation.

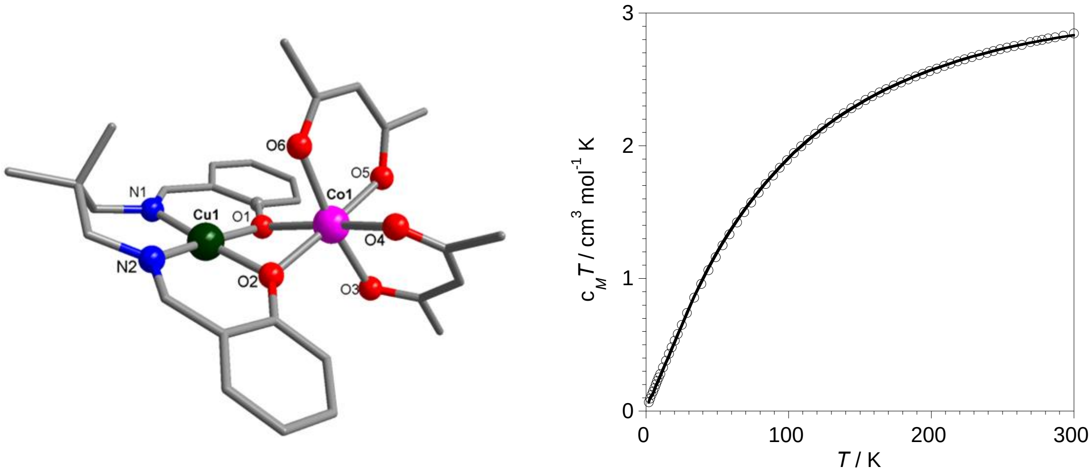
As a result, the study of the antitumor activity of compound **9** can continue, while compound **4** shows no potential to further investigate the antitumor behavior. However, compound **4** can be studied for antioxidant activities having significant hydroxyl radical scavenging activity.

Chapter IV describes the strategy for obtaining polynuclear compounds using metalloligands of Schiff bases (salen^{2-} type derivatives). The coordination of metalloligands to another metal ion is facilitated by the use of a hexafluoroacetylacetonate anion of the second metal ion. The hexafluoroacetylacetonate derivatives have an important role in obtaining homo- and heteropolynuclear systems.[19] Following the reactions, they can fully retain the $hfac^-$ groups, or an hfac- ligand can be replaced by another anionic ligand. The Lewis acidity of Mn^+ ions is high due to the hexafluoroacetylacetonate ligands, thus facilitating the coordination of other molecules, even if the coordination ability is low.

hus, a series of eight coordination compounds, characterized structurally and spectroscopically, results: $[Cu(saldmpn)Co(hfac)_2]$, **12**, $[Cu(saldmpn)Zn(hfac)_2]$, **13**, $[Cu_2(saldmpn)_2(\mu\text{-atfac})_2Zn]\cdot 2(ACN)$, **14**, where atfac = trifluoroacetate anion, $[Cu_2(saldmpn)_2(\mu\text{-atfac})_2Mn]$, **15**, $[Cu_2(saldmpn)_2(\mu_3\text{-}OCH_3)_2Cu_2(hfac)_2]$, **16**, și $[Cu_2(salpn)_2(\mu_3\text{-}OH)_3Ni_2(hfac)_2]$, **17,** $[Ni_2(valaepy)_2(hfac)_2]$, **18**, și $[Ni_2(valampy)_2(hfac)_2]$, **19.**

Compounds **12** and **13** are heterobinuclear, and for compound **12** (Figure 5) the cryomagnetic properties were investigated. The magnetic behavior of complex **12** is antiferromagnetic, the interactions between the two metal ions being mediated by the two phenoxide bridges. Data fitting led to the following parameter values: $J = -74{,}3(8)\ cm^{-1}$, $D = 79{,}6(8)\ cm^{-1}$, $g_{Cu} = 2{,}07(1)$ și $g_{Co} = 2{,}48(2)$. The curve of the experimental data and that of the theoretical data are similar.

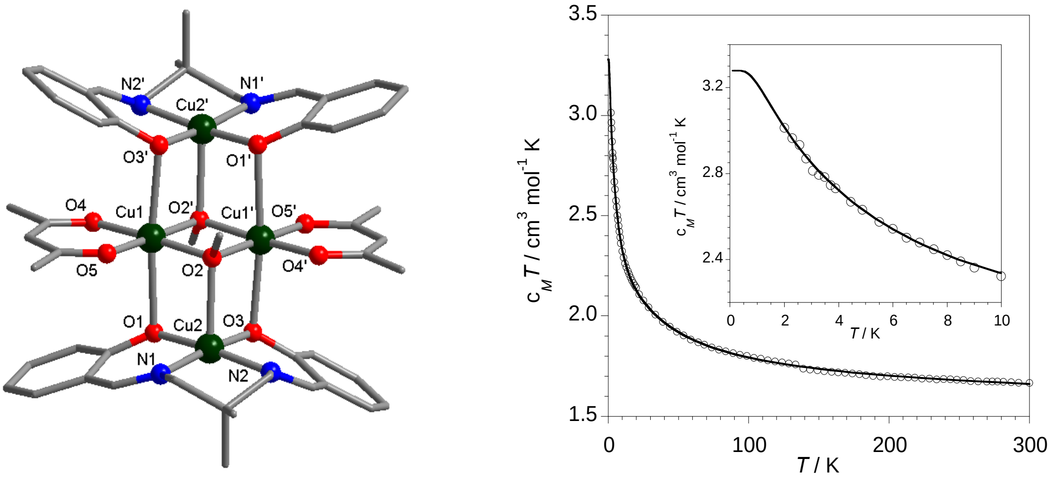
The trinuclear compounds **14** and **15** were obtained starting from the same metalloligand and the corresponding hexafluoroacetylacetonates. The trifluoroacetate ion ($atfac^-$), which functions as a bridging ligand, comes from the partial decomposition of the $hfac^-$ ions.



(a) (b)

Figure 5. (a) Structure of compound **12** and (b) $\chi_M T$ vs. T for compound **12**: (o) experimental; (-) theoretically. Hydrogen atoms were omitted for clarity.

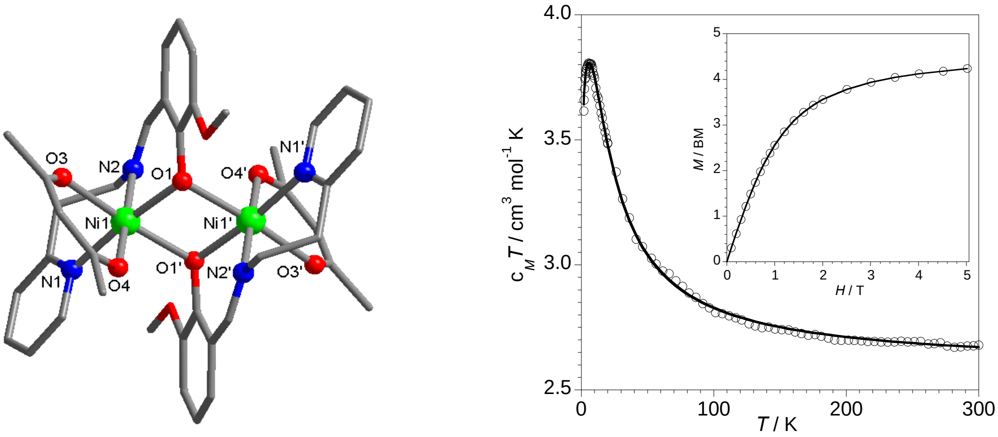
Compounds **16** and **17** are tetranuclear, presenting an interesting topology (Figure 6). For compound **16** the magnetic properties were investigated and explained. The interactions between the metal centers are ferromagnetic, being mediated by phenoxido and methoxido bridges.



(a) (b)

Figure 6. (a) Structure of compound 16 and (b) Dependence of $\chi_M T$ on temperature: (o) experimental; (-) theoretically. *Inset*: detail of the low temperature region.

Compounds **18** (Figure 7) and **19** represent another class of compounds obtained by Schiff bases derived from *o*-vanillin and diamine (2-aminomethyl- and 2-aminoethyl-pyridine). These compounds are binuclear, the double bridges being reality through the oxygen atoms in the phenoxide groups. The coupling between nickel(II) ions in compound **18** is ferromagnetic, mediated by two phenoxido bridges.



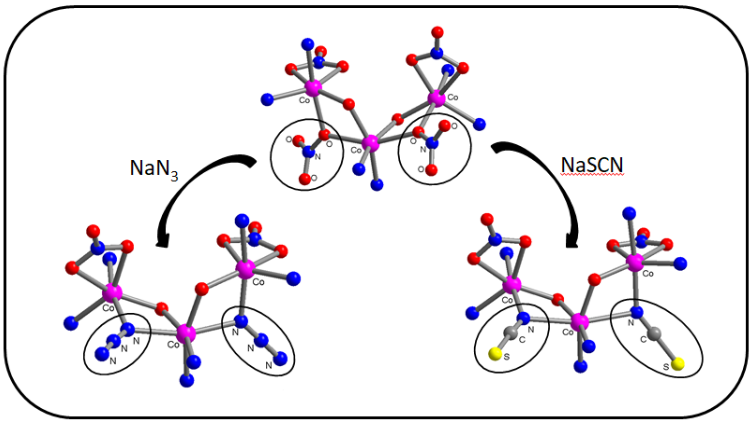
(a) (b)

Figure 7. (a) Structure of compound 18 and (b) Temperature dependence of the χ_MT product of compound 18: (o) experimental; (-) theoretically. *Inset:* field dependence of magnetization at 2.0 K.

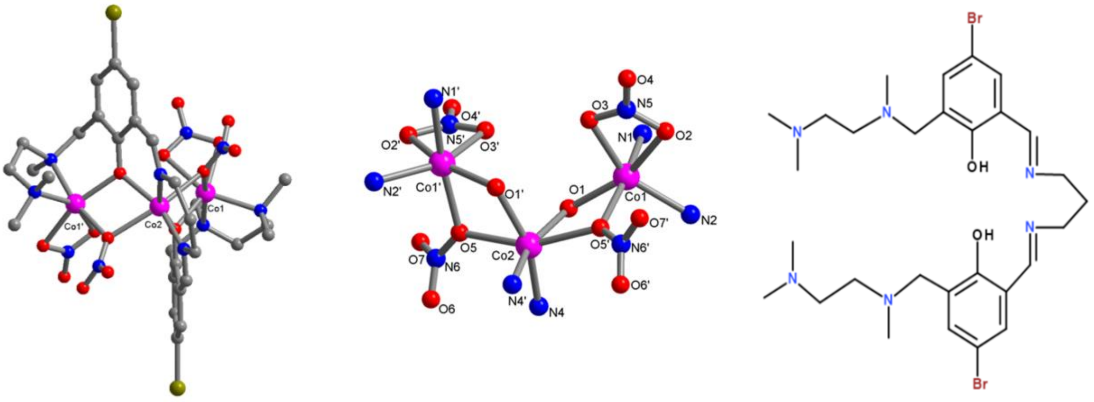
Chapter V presents interesting original results for coordination chemistry through the use in the synthesis of coordination compounds of ligands that simultaneously present Mannich and Schiff functions. For this purpose, the Mannich bases presented in Chapter III, which contain an aldehyde group, have the Schiff arm attached to them by reaction with various amines.

By coordinating the new ligands to the metallic ions of cobalt(II), nickel(II), copper(II) and zinc(II), the following compounds resulted: $[Co_3(L^1pn)(NO_3)_4]$, **20**, $[Ni_3(L^1pn)(NO_3)_4]$, **21,** $[Ni_3(L^1pn)(N_3)_2(NO_3)_2]$, **22**, $[Co_3(L^1pn)(N_3)_2(NO_3)_2]$, **23**, $[Co_3(L^1pn)(NCS)_2(NO_3)_2]\cdot(ACN)\cdot(H_2O)$, **24**, $[Ni_3(L^1pn)(NCS)_2(NO_3)_2]\cdot(ACN)\cdot(H_2O)$, **25**, $[Ni_3(L^1en)(NO_3)_4](ACN)$, **26**, $[Ni_6(L^1diox)_2(NO_3)_6]$, **27**, $[Cu(H_2L^4pn)](ClO_4)_2(H_2O)$, **28**, $[Cu_2(L^1ampol)(ClO_4)_2]$, **29**, $[Ni(HL^1ametol)(NO_3)](NO_3)$, **30**, $[Ni_4(L^1dampnol)(NO_3)_2(H_2O)_4]$, **31**, $[Ni_3(L^1amdiol)_2(MeOH)(H_2O)](ClO_4)_2(MeOH)$, **32**, $[Zn_3(L^1damdiol)(\mu\text{-}OH)_2(H_2O)](ClO_4)(H_2O)_2$, **33**, $[Cu(H_2L^4S\text{-bnaf})(ClO_4)]\cdot(ClO_4)(MeOH)$ **34,** $[Cu(H_2L^4R\text{-bnaf})(ClO_4)]\cdot(ClO_4)(MeOH)$ **35**, $[Co(H_2L^4R\text{-bnaf})(ClO_4)]\cdot(ClO_4)(MeOH)$ **36** and $[Co(H_2L^4S\text{-bnaf})(ClO_4)]\cdot(ClO_4)(MeOH)$ **37.**

In a first step, the trinuclear compounds **20** (Figure 8), **21** and **26** were synthesized, where two nitrate anions function as a bridge, each through an oxygen atom. The interesting aspect of this chapter is given by the possibility of replacing these bridges with other anions that can function as a bridge between metal ions like azide and sulfocyanide anions (Scheme 1) generating compounds **22** – **25** (structures confirmed by single crystal X-ray diffraction). The trinuclear compounds **20-26** show an angular topology influenced by metal ions, nickel(II) or cobalt(II).



Scheme 1. Schematic representation of the replacement of the two bridging nitrate ligands.



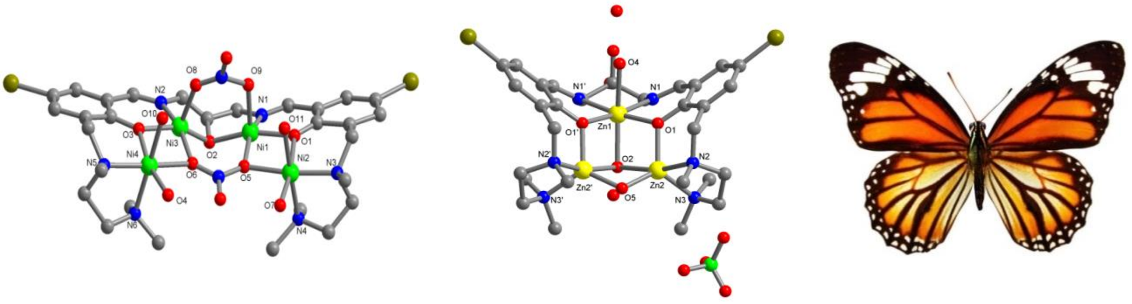
(a) (b) (c)

Figure 8. Structure of compound **20**, (b) Coordination sphere of cobalt(II) ions in compound **20** and (c) structure of ligand showing Mannich and Schiff functions. Hydrogen atoms have been omitted for clarity.

Due to the different types of bridging in compounds **20** – **25**, the investigation and interpretation of the magnetic properties led to varied results. The magnetic properties were rationalized by DFT calculations.

Compounds **22** - **24** show ferromagnetic behavior mediated by the azido bridge and the isothiocyanato bridge (**24**). For the interpretation of the magnetic properties of the three cobalt compounds, **20**, **24** and **25**, the spin-orbit coupling effect was taken into account. Regarding the nickel complexes, **21** and **22**, the magnetic behavior observed experimentally is antiferro- and ferromagnetic, respectively.

By selecting various types of primary amines functionalized with various donor groups (amino, hydroxyl) other complex combinations with interesting structures were obtained such as hexanuclear **27**, $[\mathrm{Ni^{II}}_6]$, binuclear $[\mathrm{Ni^{II}}_2]$ **29**, tetranuclear $[\mathrm{Cu^{II}}_4]$ **31**, and trinuclear $[\mathrm{Ni^{II}}_3]$ **32**, $[\mathrm{Zn^{II}}_3]$ **33** (Figure 9).



(a) (b) Fluture *Monarh*

Figure 9. (a) The butterfly structure of compound **31**, (b) the structure of compound **33** and the *Monarch* butterfly. Hydrogen atoms have been omitted for clarity.

Compounds **34-37** are isostructural, having the Schiff compartment obtained by condensation of the chiral amines S-1,1-binaphthyl-2,2-diamine and R-1,1-binaphthyl-2,2-diamine with the Mannich base. Thanks to this compartment, the complexes can be studied by circular dichroism. By varying the two arms of the ligand and the metal ions, the design of the structures is predefined and the nuclearity and properties of the complexes can be controlled.

Chapter VI represents the last chapter of the doctoral thesis. In this part, coordination compounds with an interesting structure, metallacyclophane, are presented. Metallacyclophanes are part of a category of coordination compounds that have a molecular structure similar to that of cyclophanes in organic chemistry, more precisely, two aromatic nuclei are positioned face to face by means of bridges that can be, for example, aliphatic groups. In the case of these compounds, the role of metal ions is very important in the self-assembly process, as part of the molecular architecture and its direction.

When binuclear moieties are used to construct metallacyclophanes, the intramolecular distance between the aromatic cores of the spacers can only be given by the distance between the metal ions in the binuclear units.

The ligand (H_3L) used for the synthesis of the compounds resulted from the condensation of *o*-vanillin with 2,3-diaminopropionic acid (Figure 10). The two compounds, $[NiNaL]2\bullet 2H_2O$ (**38**) and $[NiKL]_2$ (**39**), resulting from the reaction of the ligand with nickel(II) in the presence of sodium and potassium hydroxide, respectively, were characterized by X-ray diffraction on single crystal, FTIR and electron spectroscopy. DFT calculations for these compounds were performed.

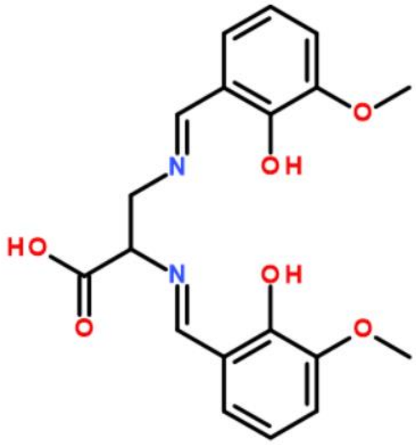
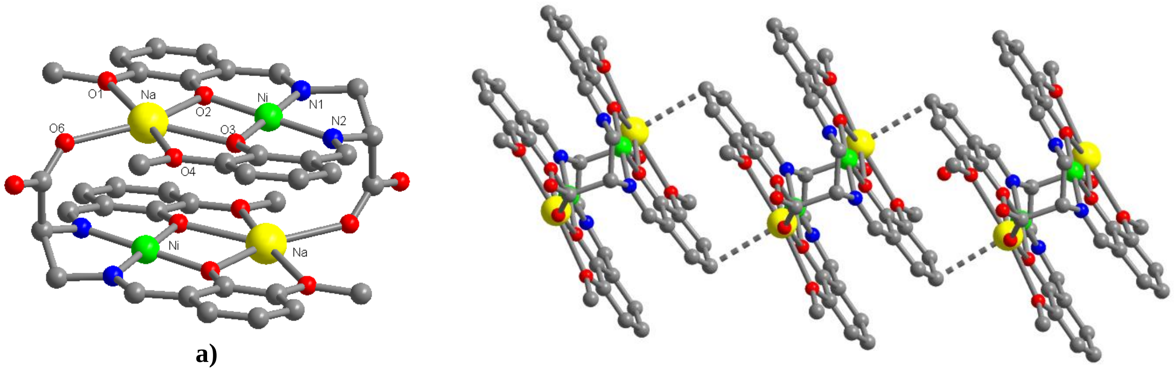


Figure 10. Structure of the H_3L ligand.

The structure of the compounds shows a Ni^{II} ion coordinated by the {N2O2} compartment and is assembled by mutual coordination of two {MNiL} units (M = Na, K). An interesting aspect of this structure is represented by the coordination geometry of the sodium ions. At first glance, this is a planar pentagonal geometry, which is rarely encountered in classical coordination chemistry, being observed for a few main group elements (ex: XeF_5^-, IF_5^{2-}).[19]

For the correct evaluation of the stereochemistry of the sodium ions, the crystal packing diagram of the compound was analyzed (Figure 11). Surprisingly, neither water nor ethanol molecules were observed to interact with the metal ions. The most important characteristic is represented by the intermolecular interactions made between the sodium ion of one molecule and the C atom of the phenyl ring of the neighboring molecule. It is also observed that the sodium ion tends towards a carbon atom, but eventually interacts with the hydrogen atom attached to it, defining an agostic interaction. The distance between two neighboring molecules is 3.04 Å.

This observation is supported by DFT calculations.



a)

b)

Figure 11. (a) Structure of compound **38**. Hydrogen atoms have been omitted for clarity. (b) Packing diagram for compound **38** showing the intermolecular interactions between the sodium ions and the carbon atoms of the aromatic rings.

In the literature, there is only one compound of a Schiff base that accommodates the nickel(II) cation in the N_2O_2 compartment and the sodium(I) cation in the O_4 compartment, which exhibits interaction between the Na^+ ion and the carbon atom of the aromatic ring of a neighboring molecule , but its structure is not metallacyclophane as in the case of compounds **38** and **39** presented in this work.

The results obtained and presented in this PhD thesis illustrate the rich chemistry of Schiff bases, Mannich bases and hybrid ligands that present the two arms, Schiff and Mannich, simultaneously. The research carried out in the PhD thesis "Homometallic and heterometallic coordination compounds obtained from Mannich-Schiff bases" resulted in **39** new compounds with discrete structures and varied nuclearities that highlight the versatility of the ligands.

The influence of Schiff and Mannich arms in the architecture and properties of the obtained compounds was observed by investigating the magnetic properties. Also, these compounds were structurally and spectroscopically characterized (by FTIR and UV-Vis spectroscopy), and for compounds **1-3**, **12**, **16**, **18**, **20-24**, **38** and **39** the elemental analysis was determined.

Referinces – selection

Chapter I

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1. M. I. Mocanu, A. A. Patrascu, S. Ionescu, M. Andruh, *J. Coord. Chem.,* **2020**, *73,* 2773;
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Conferences - selection

1. **XXXV National Conference of Chemistry**, ***2-5 October, 2018, Caciulata, Romania***

Homo- and Heterometallic Complexes Constructed from Hexafluoroacetylacetonato and Schiff Base Complexes as Building-Blocks – **Mihaela Mocanu**, Sergiu Shova, Francesc Lloret, Miguel Julve, Marius Andruh

2. **16th International Conference on Molecular-Based Magnets**, **1-5 September 2018, Rio de Janeiro, Brazil**

A new family of polynuclear complexes using mixed Schiff and Mannich base ligands – **Mihaela Mocanu**, Andrei A. Patrașcu, Francisco Lloret, Miguel Julve, Marius Andruh

3. **6th European Conference on Molecular Magnetism**, **27-31 August 2017, Bucharest, Romania**

A new synthetic approach towards polynuclear complexes using mixed Schiff and Mannich base ligands- **Mihaela Mocanu**, Andrei A. Pătrașcu, Francisco Lloret, Miguel Julve, Marius Andruh

4. **Workshop “Crystal Engineering of Multifunctional Molecule-Based Materials”, 2-6 May 2016, Sinaia, Romania**

New oligonuclear complexes derived from $M^{II}(hfac)_2$ precursors. Synthesis and characterization. - **Mihaela Mocanu**, Augustin M. Madalan, Sergiu Shova, Marius Andruh