UNIVERSITY OF BUCHAREST
FACULTY OF CHEMISTRY
DOCTORAL SCHOOL IN CHEMISTRY

PhD THESIS SUMMARY

SUPRAMOLECULAR POLYMETALLIC SYSTEMS OBTAINED BY USING COMPARTIMENTAL OR UNSYMMETRICAL LIGANDS

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2016

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Introduction

Thesis theme

The PhD thesis entitled *Supramolecular polymetallic systems obtained by using compartimental or unsymmetrical ligands* fits in the area of the coordinative and supramolecular chemistry. It is structured in two parts: a theoretical one and an original one. The theoretical part describes the self-assembly processes of the metallosupramolecular chemistry, with a highlighting on helical-type architectures. The original part of the thesis describes the synthesis of the Schiff base ligands and of the new homo- and heterometallic coordination compounds, obtained through reacting these ligands with different transitional metallic ions. Also, the spectral, structural and magnetic characterisations of the resulted systems are presented.

The thesis' first objective was the synthesis and characterisation of new metalosupramolecular helicates with 3*d*, 3*d*-3*d'* and 3*d*-4*f* metallic ions. The second one has pusued the synthesis and characterisation of new homometallic constructed from unsymmetrical Schiff base ligands and different spacers.

Directions of study:

- Synthesis of helicands derived from 3-formylsalicylic acid and *o*-vanillin
- Self-assembly of the helicands with Mn^{II}, Fe^{III}, Co^{II}, Cu^{II}, Zn^{II} ions and Fe^{III}-Co^{II}, Fe^{III}-Gd^{III} pairs for obtaining new metalosupramolecular helicates
- Synthesis of homometallic coordination compounds with unsymmetrical tetradentate Schiff base ligands derived from 3-formylsalicylic acid/*o*-vanillin and different spacers of pseudohalogenate type (thiocyanate, azide, dicyanamide) and mono- and dicarboxylic anions (nicotinate, malate, terephatalate, fumarate)
- Synthesis of homometallic systems with Schiff base ligands derived from 3-formylsalicylic acid and aminoalcohols (ethanolamine and propanolamine)
- Structural and spectral characterisation of the synthesised compounds
- Magnetic studies on systems carrying paramagnetic ions (Co^{II}, Cu^{II}, Fe^{III})

Theoretical part

Supramolecular chemistry has been defined by one of its leading proponents, Jean-Marie Lehn, as the “chemistry of molecular assemblies and of the intermolecular bond’. More colloquially this may be expressed as ‘chemistry beyond the molecule”. Other definitions include phrases such as “the chemistry of the non-covalent bond” and “non-molecular chemistry”. Originally supramolecular chemistry was defined in terms of the non-covalent interaction between a ‘host’ and a ‘guest’ molecule such as coordinative bond, hydrogen bond, *π-π stacking* and van der Waals interaction.

Research in modern supramolecular chemistry comprises not just host-guest systems but also molecular devices and machines, molecular recognition, so called ‘self-processes’ such as self-assembly and self-organisation and has interfaces with the emergence of complex matter and nanochemistry. The rapid expansion in supramolecular chemistry over the past 30 years has resulted in an enormous diversity of chemical systems, both designed and accidentally stumbled. By the term ‘preprogramming’ we understand a chemical system in which the very nature of the molecular building blocks (in terms of size, shape, symmetry and the electronic properties of their binding sites) contains all the information necessary to selectively produce the desired superstructure. The supramolecular complex assembles itself. Thus we can define self-assembly as *the spontaneous and reversible association of molecules or ions to form larger, more complex supramolecular entities according tothe intrinsic information contained in the molecules themselves* [1].

The self-assembly prosses of metal complexes into highly organized architectures (racks, ladders, grids, helicates, cages) represent one of the most important topics in supramolecular chemistry. Beyond the beauty of these supermolecules, the various topologies of the metal arrays generate interesting optical, redox, magnetic, or catalytic properties, with potential applications in nanotechnology [2].

Two components are necessary in every synthetic approach leading to inorganic supramolecular architectures: the suitable designed organic ligand and the metal ion. The spontaneous generation of the supramolecular entities is based on metal ion-directed self-assembly. In the language of supramolecular chemistry, the ligand is a programmed species, that is, an organic molecule with binding sites in a correct arrangement, with encodled information that is read by the metal ion according to its coordination algorithm (stereochemical preference) [2].

The main feature of the instructed polytopic ligand consists of the position and the high selectivity of its coordination sites (a polytopic ligand contains at least two coordination sites). The identity of the coordination sites ("pockets") is given by their ability to selectively interact with metal ions having a dominant coordination geometry. For example, tetrahedral pockets (with bidentate coordination site) will recognize metal ions with a marked preference for the tetrahedral stereochemistry (Ag^I, Cu^I), while the octahedral pockets (with tridentate coordination sites) prefer traimition metal ions such as Ni^{II}, Fe^{II} Ru^{II}, Os^{II}, which currently exhibit the octahedral coordination geometry [2].

Molecular racks [*n*]***R***, ladders [2*n*]***L***, and grids [*m*×*n*]***G*** (figure **I.1**) are examples of inorganic superstructures which are obtained through the spontaneous and correct sequential interaction between different and highly instructed components ([*n*],[2*n*], and [*m* × *n*] specify the number of the metal ions in the *R*, *L* and G structures). All these architectures are the result of the thermodynamic driving force, which leads to discrete species, rather than to coordination polymers. They have in common linear polytopic ligands as building elements, which can bridge a preestablished number of metal ions. Several ligands of this type are depicted in figure **I.2** [2].

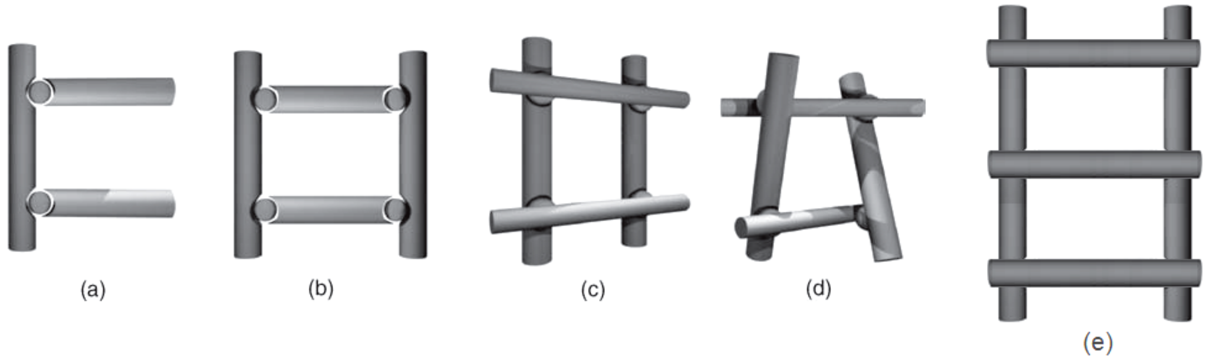


Figure I.1. Inorganic supramolecular architectures: (a) [2]***R*** rack; (b) [2·2]***L*** ladder; (c) [2×2]***G*** square grid; (d) [2×2] chiral grid; (e) [2×3] rectangular grid [2].

In the realm of supramolecular synthesis, the construction of rack, ladder, and grid architectures represents a particular case of self-assembly, which relies on the three basic levells of operation of a programmed supramolecular system: *recognition* (selective interaction of complementary components); *orientation* (building up the structure through the correct spatial disposition of the components); and *termination*, that is, the formation of the desired discrete supramolecular entity [2].

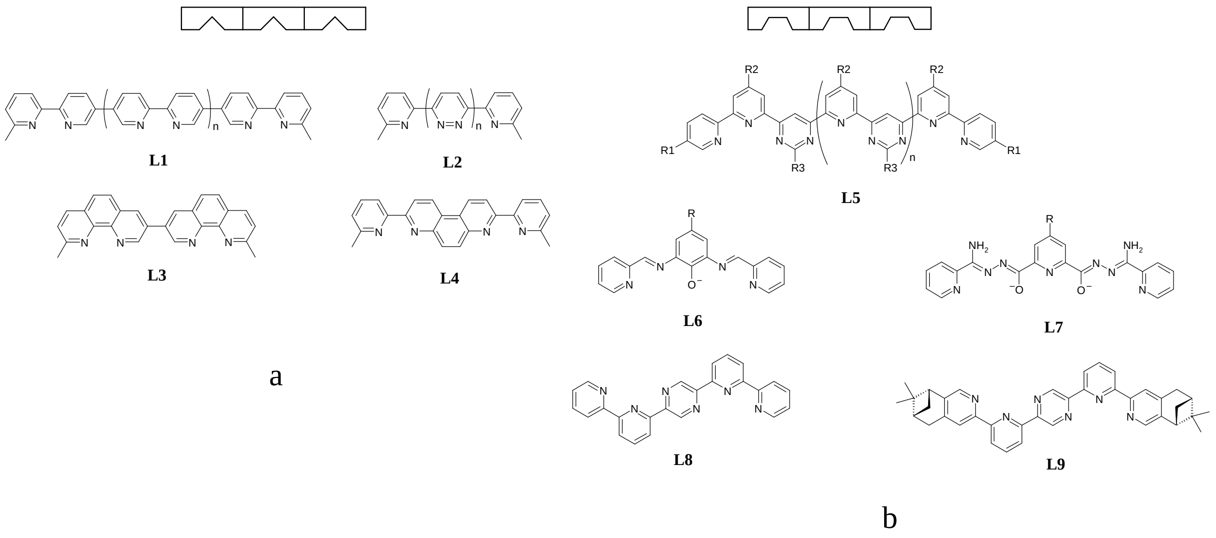


Figure I.2. Linear ligands used to generate racks, ladders and grids: (a) polytopic ligands with tetrahedral pockets; (b) polytopic ligands with octahedral pockets.

One of the most fascinating aspects of supramolecular chemistry is the spontaneous formation of organized architectures from successive molecular recognition processes between various components. The selectivity of the self-assembly process depends on (1) the stereoelectronic molecular informations encoded in the components (i.e., the intrinsic information) and (2) the external conditions used for the reading, the recognition and the expression of this information in the final supramolecular edifices [35].

There is a large variety of coordination compounds whose molecular structure may be described as helical. Pseudotetrahedral complexes possessing two unsymmetrical bidentate AB-type ligands coordinated to a central metal ion $[M(AB)_2]$ (figure **I.32a**) or pseudooctahedral complexes $[M(AB)_3]$ or $[M(AA)_3]$ (figure **I.32b**) correspond to helical complexes since the absolute configuration of the metal ion produces right-handed (*P*) or left-handed (*M*) helicity along their principal C_2 and C_3 axes [35].

a b

Figure I.32. Absolute configurations and helicities of (a) bis-chelate complexes viewed down the *C*2 axis and (b) tris-chelate complexes viewed down the *C*3 axis.

Although the term *helicate* appeared only in 1987, a series of double- and triple stranded polynuclear coordination complexes have been obtained previously, such as the $[Cu_2(\mathbf{L26})_3]^{4+}$ binuclear compound (figure **I.33**) with a helical structure, prepared by Harris and McKenzie [37], which could be considered the first triple stranded helicate.

L26

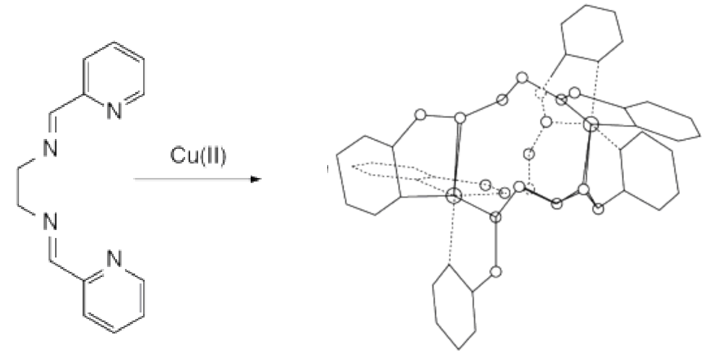


Figure I.33. The first triple stranded helicate $[Cu_2(\mathbf{L26})_3]^{4+}$ [37].

Inspired by previous investigations on the electrochemical behavior of intertwinned dimeric Cu(I) complexes, Lehn and coworkers selected the noncovalent Cu^{I}–N bonds for the programmed connection of two covalent helical strands around a central axis defined by a line of regularly spaced metal ions in the complex $[Cu_3(\mathbf{L27})_2]^{3+}$ (figura **I.34**) [38]. This double-stranded helix was the first recognized member of what has become later a novel and large family of polynuclear coordination complexes, termed helicates.

L27

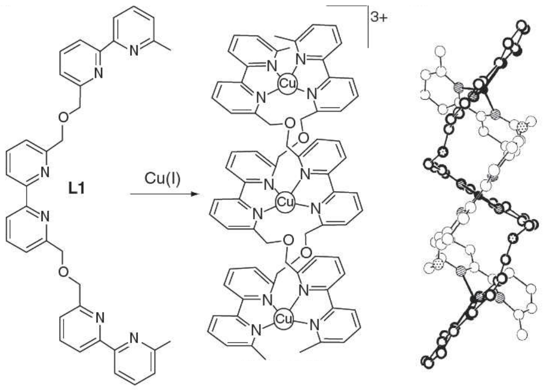
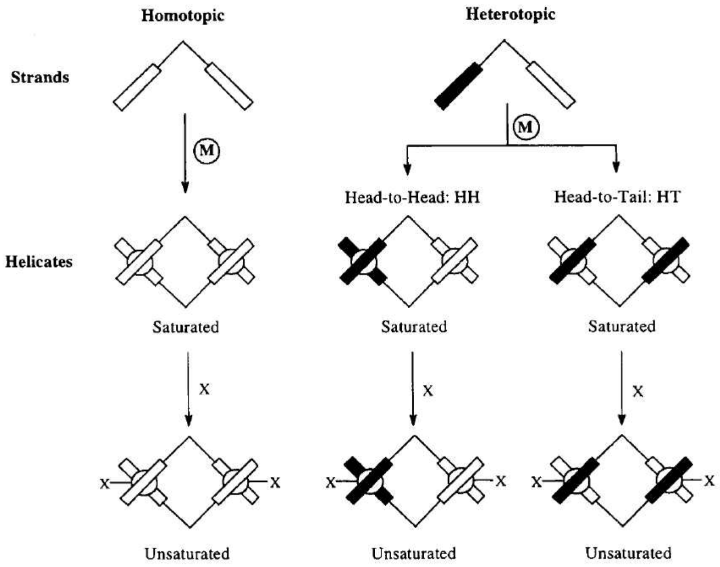


Figure I.34. Self-assembly of the trinuclear saturated homotopic double-stranded helicate $[Cu_3(\mathbf{L27})_2]^{3+}$.

The term *helicate* was introduced by Lehn and coworkers in 1987 for the description of a polymetallic helical double-stranded complex. It is formed of the word *helix* (ελιξ, greek: spiral) and the suffix -*ate*, characterizing host-guest complexes between (pre)organized receptors and metal ions in the same way as as coron*ates* or crypt*ates*. The importance of the helicates is related to the development and the understanding of self-processes in supramolecular chemistry. The spontaneous generation of the helix $[Cu_3(\mathbf{L27})_2]^{3+}$ was perceived at that time as a self-assembly process similar to those studied in biology. Intense research activities have been focused on this new field in order to explore and apply its power of design and control for the selective preparation of complicated organized architectures [35].

The helicates can be classified by taking into account the following characteristics [35]:

- the number of coordinated strands are associated with *single*-, *double*-, and *triple*-stranded helicates possessing respectively, one, two and three strands wrapped about the metal ions.
- Identical coordinated strands correspond to *homostranded* helicates while the presence of different strands leads to *heterostranded* helicates which exist in two isomeric forms according to the orientations of the coordinated binding units (head-to-head, HH, or head-to-tail, HT) (scheme **I.8**);
- Each category is further split into *saturated* helicate when the stereochemical requirements of the metal ions are fulfiled by the donor atoms of the strands and *unsaturated* when supplementary ligands complete the coordination sphere of the metals (schema **I.8**).



Scheme I.8

Dinuclear saturated homotopic helicates possess at least one coordinated strand with a $C2$ axis or a symmetry plane passing through the ligand and perpendicular to the helical axis. They result from the assembly of symmetrical organic ligands possessing two identical binding units (*homotopic* = same denticity, same connectivity, same donor atoms) disposed along the strand with metal ions whose stereochemical requirements are completely fulfilled (saturated) by the coordinating units of the organic strands. Homotopic helicates with $n \geq 3$ result when (1) at least one coordinated strand possesses a $C2$ axis or a symmetry plane perpendicular to the helical axis and (2) the binding units along the strands are similar and separated by similar spacers [35]. When the coordinated strands in a dinuclear helicate do not possess a $C2$ axis or a symmetry passing through the ligand and perpendicular to the helical axis, the resulting helicates are heterotopic. Stereoisomerichelicates result from the various possible arrangements of the strands: for a double-stranded helicate, two different orientations must be considered: (1) a head-to-head arrangement (HH) where the identical binding units of each strand are coordinated to the same metal ion and (2) a head-to-tail arrangement (HT) corresponding to the coordination of the different binding units of each strand to the same metal. For higher nuclearities, the existence of different coordinated binding units along the strand is a sufficient condition to produce a heterotopic helicate [35].

Original part

Within the PhD research activity, two main directions were pursued. *The first direction* was the synthesis of polymetallic helicates constructed from Schiff base helicands derived from 3-formylsalicylic acid and *o*-vanillin. Ten such compounds were obtained, which were characterised structurally through X-ray diffraction and spectroscopically through IR and UV-vis-NIR studies.

The H_2vanet helicand resulted from the 2 : 1 condensation reaction between *o*-vanillin and 4,4’-diamino-diphenylether provide three new double stranded helicates containing Co^{II}, Cu^{II}, and, respectively, Zn^{II} ions (compounds **1**, **2** and **3** respectively). Within the three compounds, the metal ions display distorted tetrahedral coordination geometries. Compound **1** exhibits an interesting crystal packing, as helicates of the same chirality are disposed in supramolecular chains, which in turn generate channels hosting the solvent molecules.

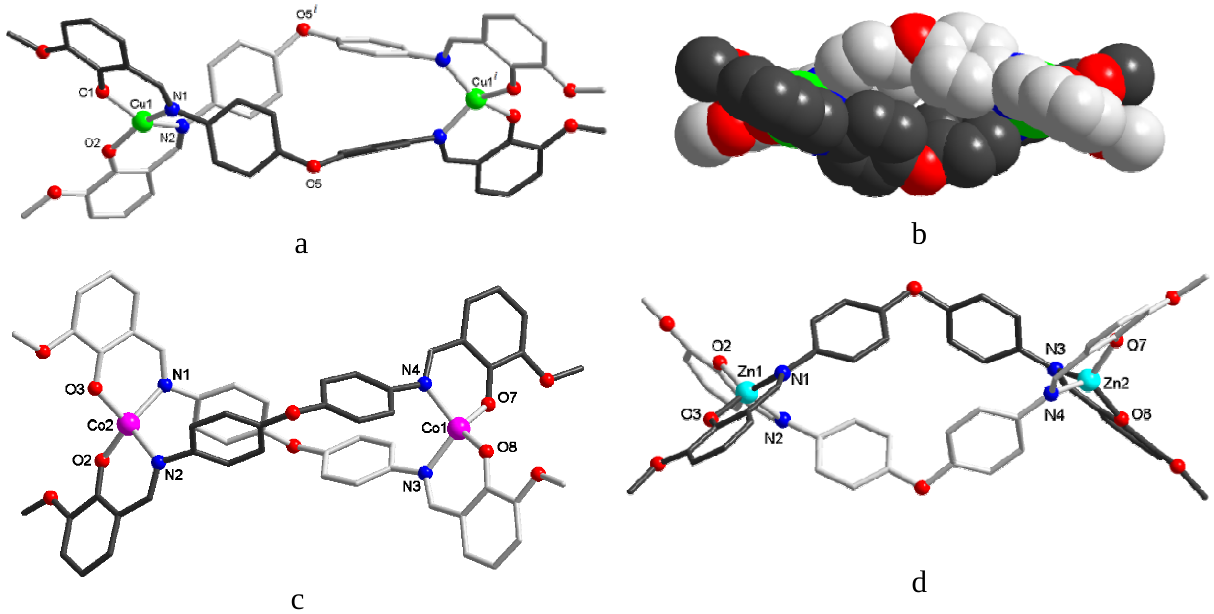
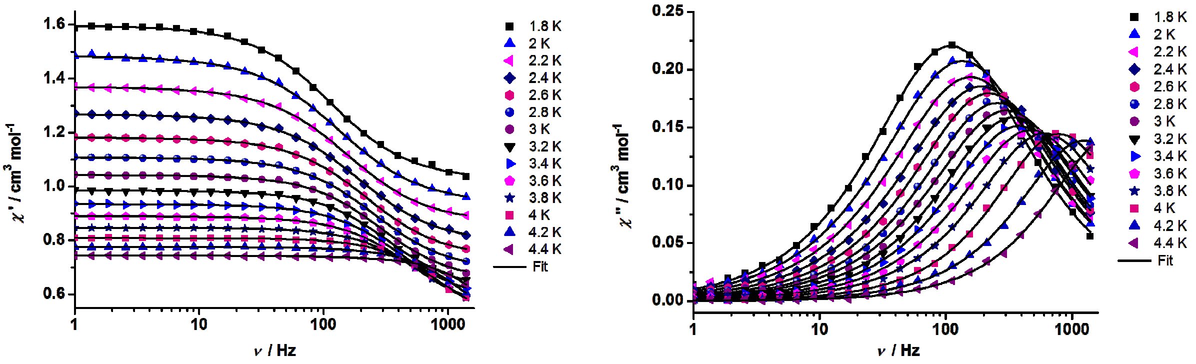


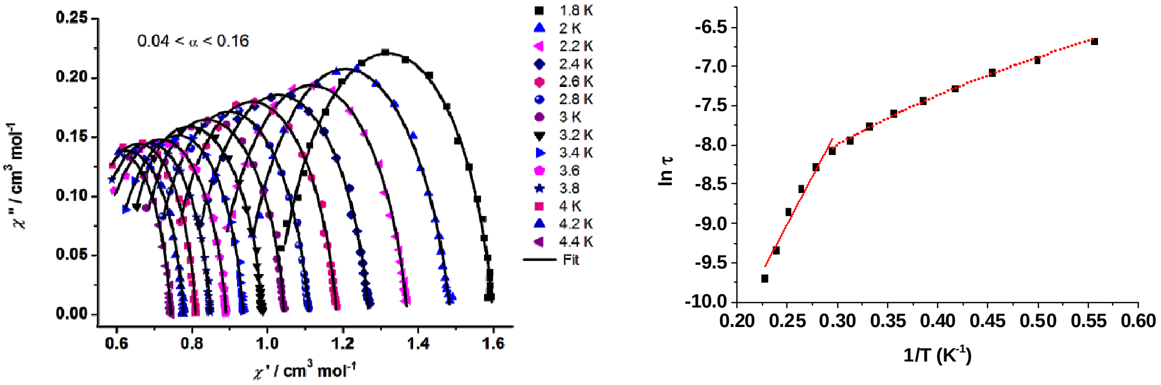
Figure 1. Crystal structures of compounds (a, b) **1** (in two representations, *i*= *1.5-x, 1.5-y, z*), (c) **2** and (d) **3**.

The most interesting compound, from the magnetic point of view, is the cobalt(II) helicate **2**: EPR spectroscopy indicates an easy axis type magnetic anisotropy, with some rhombicity, for both CoII centers, and dynamic susceptibility measurements provide evidence that the magnetization relaxes slowly under the application of a small dc field (figure **3**). To the best of our knowledge, this is the first example of a helicate containing a transition metal ion showing this behavior. Dilution experiments demonstrated that the slow relaxation cannot be attributed to the magnetic anisotropy barrier, even if the magnetic data analysis unequivocally shows this is present, but rather to phonon bottleneck effects.



a b

Figure 2. Frequency dependence of the in-phase ac susceptibility (χ') and of the out-of-phase ac susceptibility (χ'') of **2** collected at temperature intervals of 0.2 K between 1.8 and 4.4 K.



a b

Figure 3. (a) Cole-Cole plot for **1** at different temperatures with an applied dc field of compound **2**; solid lines represent the best fit. (b) Arrhenius plot of the temperature dependence of the relaxation rate of compound **2**. High temperature data were fitted to a linear equation (continuous line), while low temperature one were fitted to a $\tau = aT^n$ law (dotted line).

The zinc helicate **3** shows luminescence in solution, which depends strongly on the nature of the solvent. The highest quantum yield (4.47%) was observed in chloroform, with a life time of 4 ns (figure **4**).

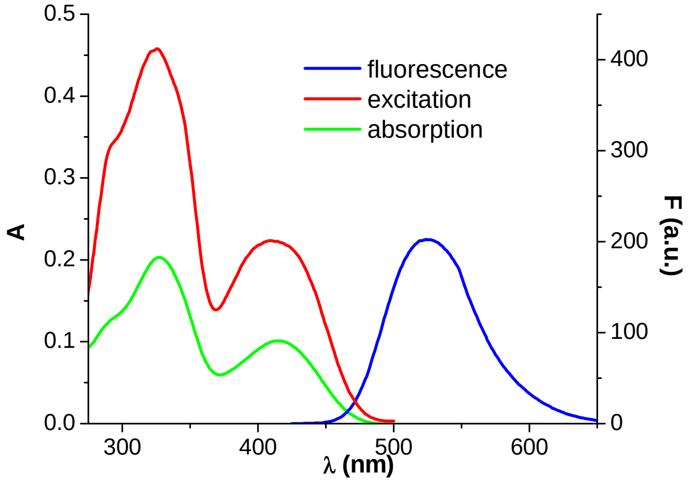
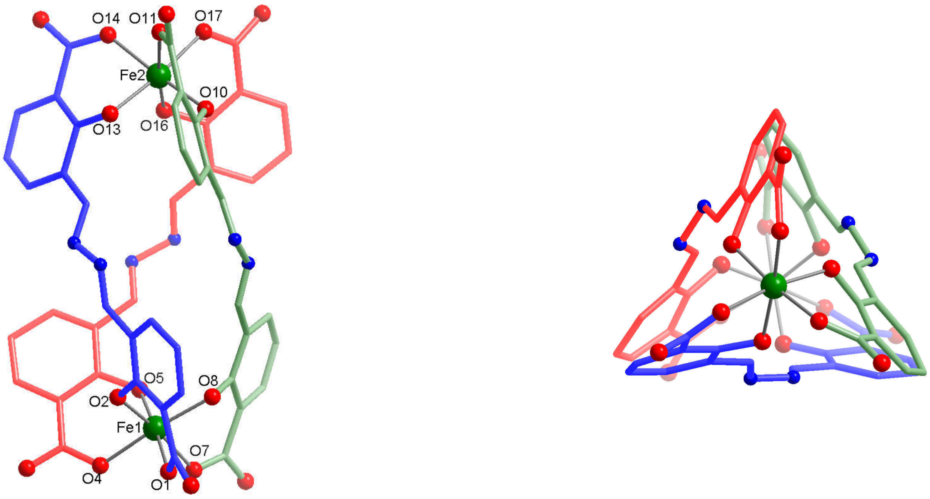


Figure 4. Absorption, excitation and fluorescence spectra of compound **3** in chloroform. λ_{ex} = 416 nm; λ_{em} = 525 nm.

By using the H_4fsahy helicand, prepared from the condensation reaction between 3-formylsalicylic acid and hydrazine in a 2:1 molar ratio, a series of homo- and heterometallic helicates (compounds **4-10**) were constructed with different 3*d* (Cu^{II}, Fe^{III}, Co^{II}, Mn^{II}), 3*d*-3*d*' ($Co^{II}Fe^{III}$) and 3*d*-4*f* ($Fe^{III}Gd^{III}$) metal ions.

X-ray diffraction measurements on compound $[Cu_{2,14}(H_{1,86}fsahy)_2(DMF)_2]$ (**4**) at low temperature have indicated that this compound exhibits two different crystalographic components, which are present in a 3 : 1 proportion in the crystal of **4**. Both components consist of double unsaturated copper(II) helicates. The main component is in turn composed of a statistical mixture of 4 molecular species, namely one binuclear, two binuclear and one tetranuclear species, while the minor component consists of only a binuclear species. Thus, it has been demonstrated that when reacted with H_4fsahy helicand, the copper ions coordinate preferentially in the internal sites of the helicand, rather than in the external ones. Both components exhibit three-dimensional networks with channels of cca 13 × 7 Å, hosting solvent molecules.

The self-assembly of H_4fsahy helicand with Fe^{III} metal ions has led to a three-dimensional coordination polymer $_{\infty}^{3}[Fe_2(fsahy)_3Na_6(H_2O)_{12}]$ **5** (figure **5**), consisting of binuclear triple $[Fe_2(fsahy)_3]^{6-}$ helicates connected through sodium ions. The Fe^{III} ions are coordinated only by the external sites of the ligands and have distorted octahedral coordination geometries. In the crystal packing, layers of helicates are formed, which are separated by layers of sodium ions and water molecules.



a b

Figure 5. (a) The $[Fe_2(fsahy)_3]^{6-}$ triple helicate, viewed along two different directions. The *M* enantiomer was represented.

The reaction of the H_4fsahy helicand with the Co^{II} ions has led to two triple helical systems $_\infty^3[Co_4(fsahy)_3Na_4(H_2O)_4]$ (**6**) şi $_\infty^2[Co_5(fsahy)_3Na_2(H_2O)_{11.6}]\cdot DMF$ (**7**) (figure **6**), depending on the metal : ligand molar ratio. Compound **6**, obtained by using a 3 : 4 ratio, consistes of $[Co_4(fsahy)_3]^{4-}$ triple tetranuclear helicates, connected by sodium ions into a 3D network. The four Co^{II} metal ions exhibit intermediate coordination geometries, between octahedral and trigonal prism.

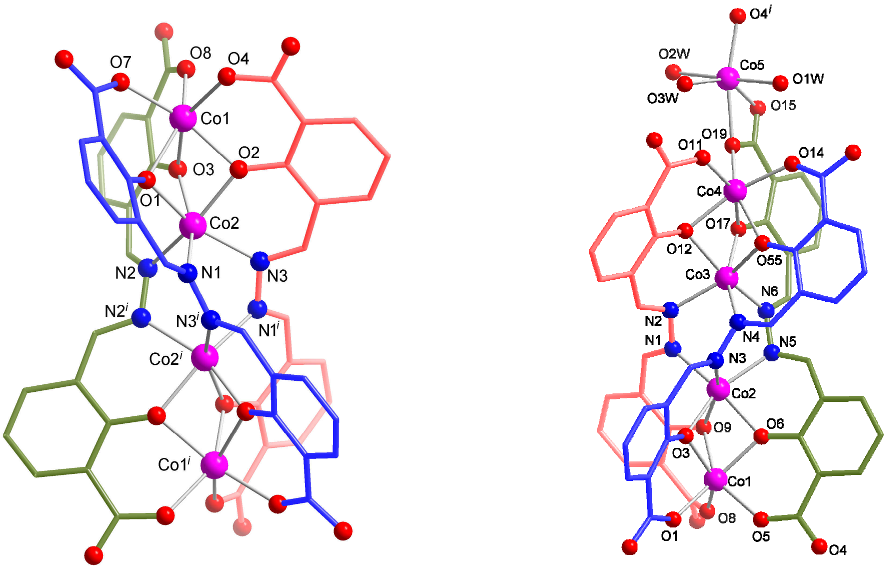
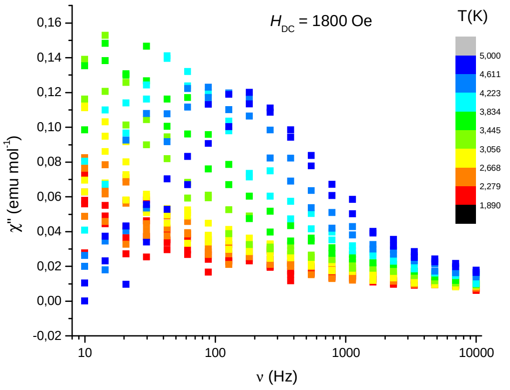


Figure 6. The triple helical $[Co_4(fsahy)_3]^{4-}$ unit in compound **6** (left, symmetry code *i* = *x, -y, 2-z*) and the repetitive $\{Co_5\}$ unit in compound **7** (right, symmetry code *i* = *0.5+x, 0.5-y, -0.5+z*).

When using an excess of Co^{II} ions, the compound **7** was obtained, consisting of 1D chains in which $[Co_4(fsahy)_3]^{4-}$ triple helical units are connected by the additional Co^{II} ions. The chains are further connected by sodium ions, leading to a 2D network. The magnetic measurements at low temperatures have indicated for compound **6** an antiferromagnetic coupling between the four metal ions within the $[Co_4(fsahy)_3]^{4-}$ units, while for compound 7 a substantial paramagnetism, in agreement with the odd number of spins. The *ac* measurements for the latter compound proved to be interesting, since the system shows a non-zero χ'' signal both in zero field and in applied field. No relevant dependence on the applied field is observed (figure **7**).



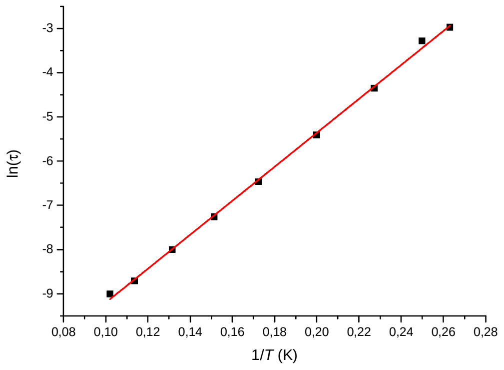
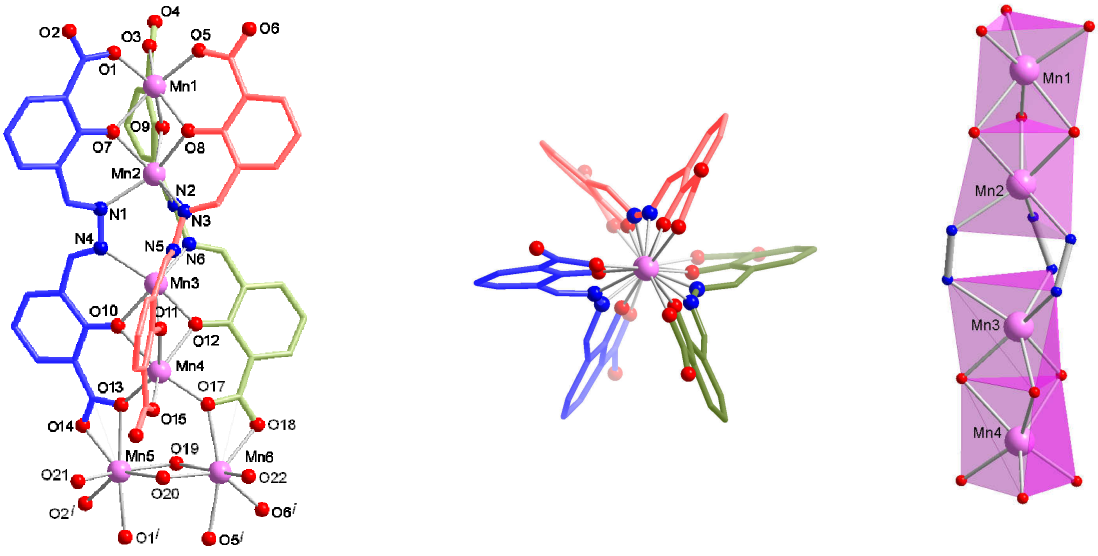


Figure 7. (left) Temperature dependence of χ'' *vs T* in an applied field of 1800 Oe, up to 5 K and (right) the Arrhenius plot for compound **7**.

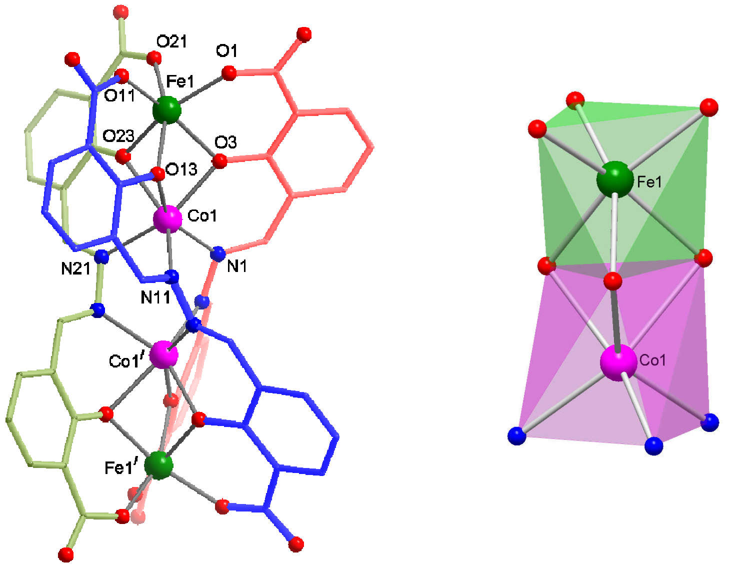
The same helicand (deprotonated with triethylamine) when reacted with Mn^{II} ions has led to compound ${}_{\infty}^{1}[Mn_6(fsahy)_3(H_2O)_4]\cdot 8H_2O$ **8**, in which tetranuclear $[Mn_4(fsahy)_3]^{4-}$ triple helial units are connected through pairs of manganes(II) ions (figure **8**). The four metal ions within the helical unit have a coordination number of 6 and a slightly distorted trigonal prism geometry, while the two manganese(II) ions that connect the helicates have a coordination number of 7 and a pentagonal bipyramid geometry. Chains are thus formed, in which the helicates shows alternantly opposite chiralities, as in compound **7**. In the crystal packing, the chains are parallel.



a b c

Figure 8. (a,b) Crystal structure of compound **8,** viewed along two different directions and (c) coordination polyhedra around Mn1–Mn4 ions. (*i*) *-1+x, 1-y, -0.5+z.*

The ability of the H_4fsahy ligand to coordinate simultaneously to two different metal ions has been demonstrated by its self-assembly with the Co^{II}-Fe^{III} pair, that has led to the compound ${}_{\infty}^{1}[Fe_2Co_2(fsahy)_3Na_2(H_2O)_4(EtOH)_2]\cdot 3H_2O$ **9** (figure **9**). The crystal structure of **9** consists of tetranuclear triple-stranded dianionic $[Fe_2Co_2(fsahy)_3]^{2-}$ helicates connected through Na ions. The Fe-Co ratio was confirmed by elemental chemical analysis as well as by mass spectrometry (fast atom bombardment, FAB). Two Co^{II} and two Fe^{III} ions are accommodated into the resulting triple helicate architecture. The metal ions display different coordination environments: the Co^{II} ions are coordinated by the inner pockets of the helicand and display a distorted octahedral stereochemistry, while the Fe^{III} ions are coordinated by the peripheral ones and display a distorted trigonal-prismatic geometry. Homochiral $[Fe_2Co_2(fsahy)_3]^{2-}$ anions are connected by pairs of Na ions, resulting in a chiral 1-D coordination polymer (Figure 2). The space group is centrosymmetric, so chains with opposite chiralities are present in the crystal. Magnetic measurements have revealed a moderate antiferromagnetic coupling between the Fe^{III} and Co^{II} ions (J_1^z = -44.5 cm^{-1}) connected through fenoxo bridges and a weaker antiferromagnetic interaction (J_2^z = -2.8 cm^{-1}) between the two Co^{II} ions through the $\mu_{1,2}$-diazino bridges.

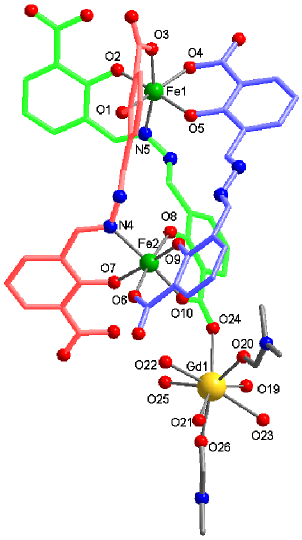


a b

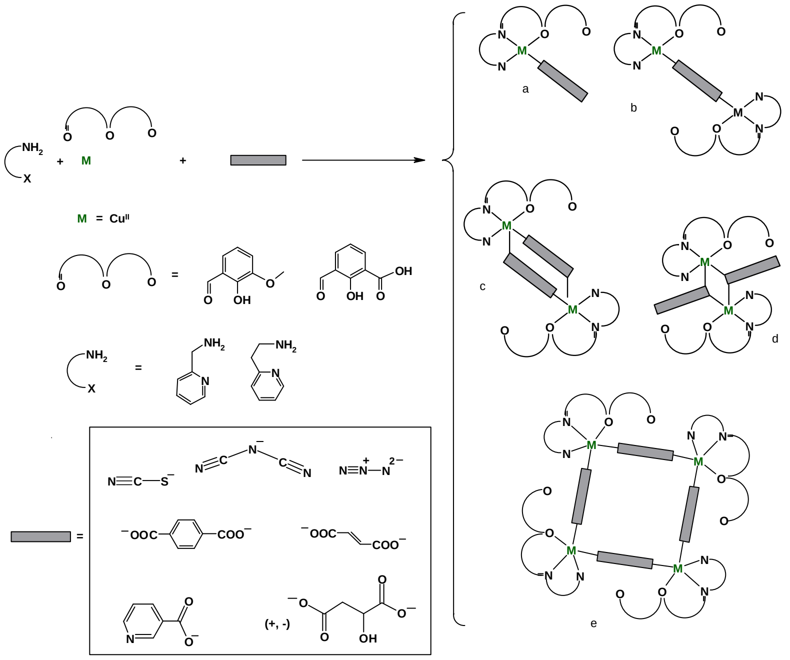
Figure 9. (a) Crystal structure of $[Fe_2Co_2(fsahy)_3]^{2-}$ unit and (b) the coordination polyhedra around the metal centers. Symmetry code*: i = -x, y, 0,5-z.*

In an attempt to obtain a 3*d*-4*f* helicate, the H_4fsahy helicand was reacted with an equimolar mixture of Fe^{III} and Gd^{III} ions. In the crystal structure of the resulted system, $[Fe_2(fsahy)_3Gd(H_2O)_5(DMF)_2]\cdot 4H_2O$ **10** (figure **10**), the ligands wrap around only two Fe^{III} ions, leading to a homobinuclear helical $[Fe_2(fsahy)_3]^{3-}$ anion, which coordinates through a carboxylic group to a complex $[Gd(H_2O)_5(DMF)_2]^{3+}$ cation. Each of the Fe^{III} ions has a distorted octahedral geometry and is coordinated by one internal and two external sites of the ligands. The gadolinium(III) ion has a coordination number 8 and a square antiprism coordination geometry

Figure 10. Crystal structure of compound **10**.



The second research direction within the PhD thesis has pursued the synthesis of homometallic systems by using unsymmetrical Schiff base ligands derived from 3-formylsalicylic acid/*o*-vanillin and different spacers. Nine coordination compounds were obtained with Hvalampy şi H_2fsaaepy (prepared by condensation reaction between *o*-vanillin and 2-(aminoethyl)pyridine, and between 3-formylsalicylic acid and 2-(aminomethyl)piridine, respectively), copper(II) ions and spacers such as pseudohalogenate type-anions (thiocyanate, azide, dicyanamide) and mono- and dicarboxylic anions (nicotinate, malate, terephatalate, fumarate) (scheme **1**).



Scheme 1

By reacting the thiocyanate anion, NCS^-, with the $[Cu(valampy)]^+$ and $[Cu(Hfsaaepy)]^+$ units, the compounds $[Cu(valampy)(NCS)(DMF)]$ **11** and $[Cu_2(Hfsaaepy)_2(NCS)_2]$ **12** were obtained respectively.

The crystal structure of compound **11** consists of mononuclear units, in which the thiocyanate anion coordinates in a terminal monodentate mode and in the basal plane of the copper(II) ion. The apical position is occupied by a DMF molecule. In **12**, two NCS^- anions coordinate in a $\mu_{1,3}$ bridging mode between two copper(II) ions, leading to a binuclear system.

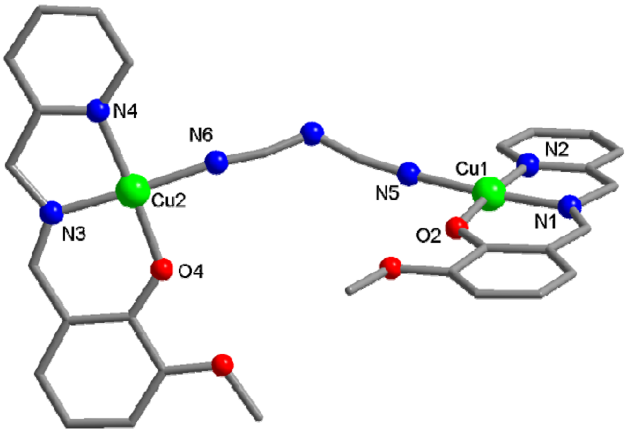


Figure 11. Crystal structure of compound **13**.

By using the dicyanamidate anion, two binuclear compounds, $[Cu_2(valampy)_2(dca)](ClO_4)$ **13** and $[Cu_2(Hfsaaepy)_2(dca)_2]$ **14**, were obtained, in which this anion acts as a $\mu_{1,5}$ bridging ligand. In compound **13** (figure **11**), the two Cu^{II} ions are bridged by a single dca^- ligand and show a distorted square-planar geometry, while in compound **14**, the metal ions are bridged by two dca^- anions and exhibit a square-pyramidal geometry. The latter compound was magnetically characterised, the study of these data indicating a weak antiferromagnetic coupling between the copper(II) centers (J = -1,13 cm^{-1}) (figure **12**).

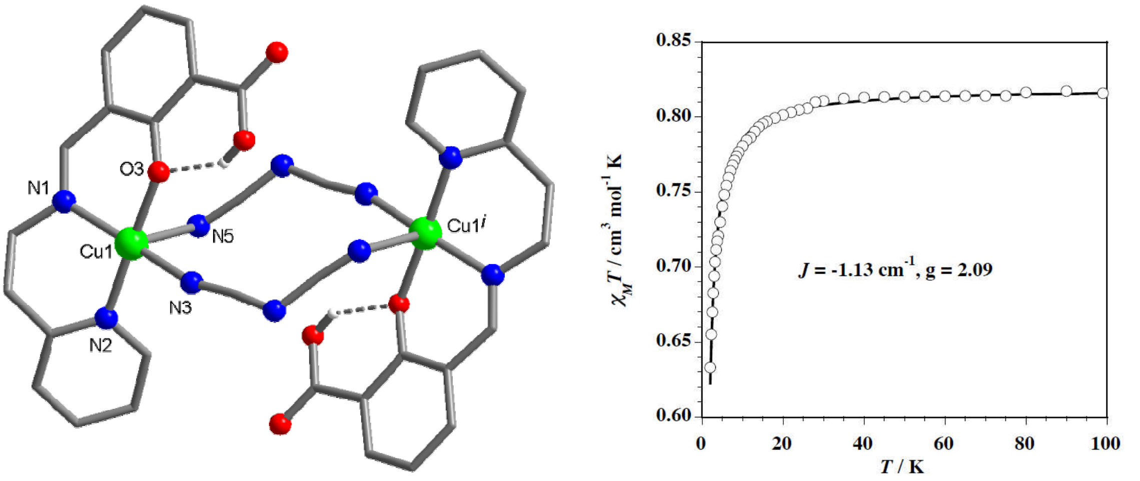


Figure 12. (left) Crystal structure of compound **14**. Symmetry code: (*i*) *2-x, 1-y, -z*; (right) $\chi_M T$ vs T plot for compound **14**.

The reaction of azide anion with the {Cu(Hfsaaepy)} unit has also led to a binuclear system $[Cu_2(Hfsaaepy)_2(N_3)_2]$ **15**, in which the two N_3^- ligands coordinate as $\mu_{1,1}$ bridges. The magnetic data have indicated a weak antiferromagnetic coupling between the copper(II) ions (J = -2,14 cm^{-1}).

Using the anions of mono- and dicarboxylic acids, such as nicotinate, malate, terephtalate and fumarate, a series of mono-, bi- and tetranuclear systems with Cu^{II} ions was obtained: $[Cu_4(Hfsaaepy)_4(NA)_4]$ **16**, [Cu(Hfsaaepy)(Hmal)] **17**, $\{[Cu(valampy)(H_2O)]_2(ter)\}\cdot H_2O$ **18** şi $[(Cu_2(valampy)_2)_2(H_2O)_2(fum)](ClO_4)_2\cdot 2H_2O$ **19**.

Compound **16** has a tetranulear structure consisting of four {Cu(Hfsaaepy)} units connected through four bridging nicotinato anions (figure **13**). The copper(II) ions lie on the vertices of a parallelogram with sides measuring 7,23 and 7,99 Å. The study of the magnetic data for this compound has indicated a very weak antiferromagnetic coupling between the metal ions (J = -0,045 cm^{-1}, g = 2,10) (figure **13**).

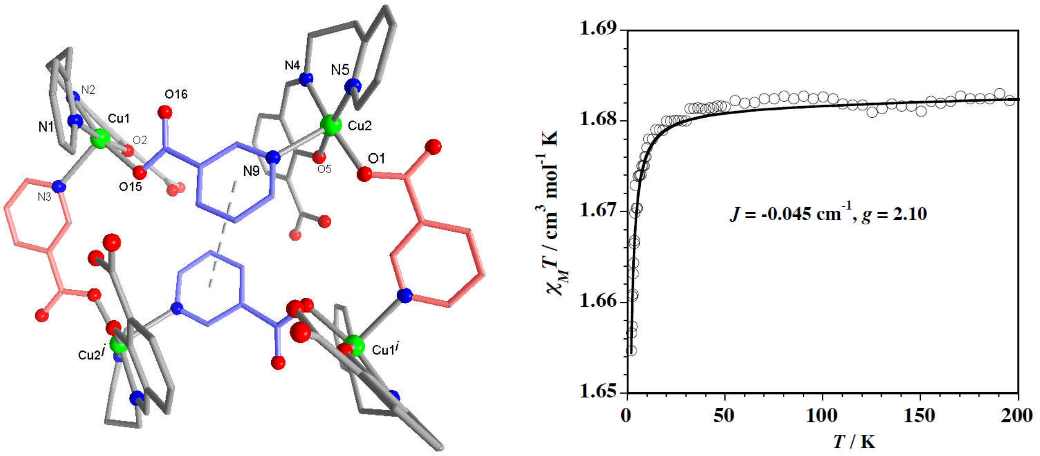


Figure 13. (left) Crystal structure of compound **16**. Symmetry code: (*i*) *1-x*, *1-y*, *-z*; (right) $\chi_M T$ vs. T plot for compound **16**.

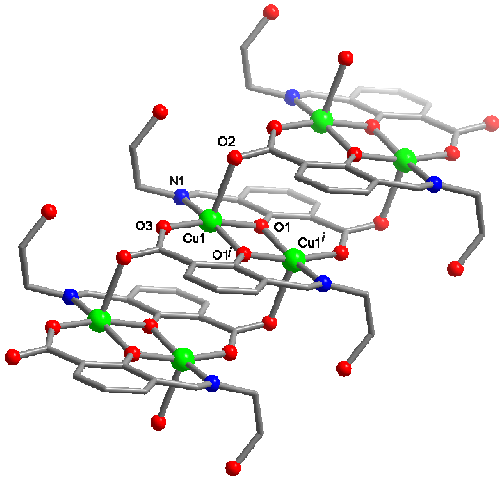
The crystal structure of compound **17** consists of mononuclear [Cu(Hfsaaepy)(Hmal)] units, in which the malate anion coordinates in a bidentate chelating mode to the copper(II) ion through the α deprotonated carboxylic group and undeprotonated hydroxilic group. The crystal packing is sustained by multiple hydrogen bonds which involve the undeprotonated/ deprotonated carboxylic groups and the hydroxilic groups of the malate anions.

Compound **18** is a binuclear system consisting of two {Cu(valampy)(H_2O)} units connected by a terephtalate anion which coordinates in a *trans* bis-monodentate mode. At supramolecular level, this compound shows a series of non-covalent interactions that lead to chains and layers.

A special case is that of compound **19**, in which the fumarate anion coordinates in a less usual mode (bis-bidentate μ_4 bridge) linking two binuclear {(Cu_2(valampy)$_2$(H_2O)} units and leading to centrosymmetric tetranuclear units.

Two homometallic compounds $^1_\infty${Cu(Hfsamea)} **20** and [Dy(H_2fsapa)$_4$](H_3O)(H_2O) **21** with unsymmetrical Schiff base ligands derived from 3-formylsalycilic acid and aminoalcohols (ethanolamine and propanolamine) were also obtained. The structure of the first compound **20** (figure **14**), consists of chains in which binuclear [Cu_2(Hfsamea)$_2$] units are interconnected through carboxylic groups coordinated at the apical sites of the Cu^{II} ions. At supramolecular level, six adjacent chains are disposed in a hexagonal manner, leading to the formation of hexagonal channels with diameters of ~8 Å. X-ray diffraction and TG studies have indicated the absense of guest molecules within the channels.

Figure 14. Crystal structure of compound **20**. Symmetry code: (*i*) *2-x*, *-y*, *1-z*.



In the crystal structure of compound **21**, neutral mononuclear [Dy(H_2fsapa)$_3$(H_2fsapa)] units are present, along with water molecules. The ligands coordinate with (O,O) sites to Dy^{III} ion, which exhibits a coordination numer of 8 and a distorted square antiprism geometry (figure **15**). In the crystal packing, hydrogen bonds are established between the undeprotonated aminoalcohol groups, carboxylate groups and water molecules.

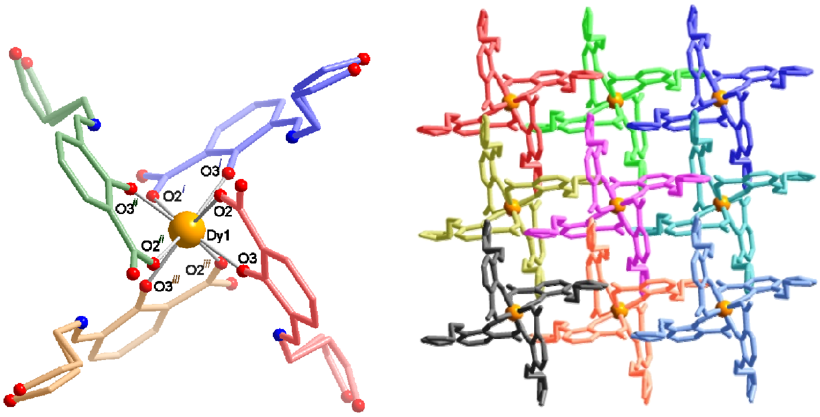


Figure 15. (left) Crystal structure of the mononuclear [Dy(H_2fsapa)$_3$(H_3fsapa)] unit and (right) detail of the crystal packing viewed along the *c* axes, in compound **21**.

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