UNIVERSITY OF BUCHAREST
FACULTY OF CHEMISTRY
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DOCTORAL THESIS SUMMARY

NEW SYNTHETIC ROUTES IN THE 3*d*-4*f* MAGNETIC CLUSTER CHEMISTRY

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NEW SYNTHETIC ROUTES IN THE 3*d*-4*f* MAGNETIC CLUSTER CHEMISTRY

The topic of this thesis belongs to both fields of coordinative chemistry and molecular magnetism. The former reffers to the synthesis of ligands and complex systems playing the role of precursors for magnetic molecular systems while the latter aims to define and study the magnetic and magnetocaloric properties elicited by these systems.

In brief, the scope of the research reported in this thesis is the synthesis of heteropolynuclear 3*d*-4*f* magnetic coordination compounds with high nuclearity using different organic ligand families.

Objective

The development of new synthetic routes towards 3*d*-4*f* cluster type systems characterized by high nuclearity to allow the study of the nanomagnetic behaviour (slow magnetic relaxation) and the magnetocaloric effect was targeted.

Main research areas

The research carried out during the 3 year doctoral tenure can be divided into several research streams:

- synthesis of new classes of heterododecanuclear 3*d*-4*f*, $[M^{II}_6Ln^{III}_6]$ coordination complexes for the study of the magnetic interaction between 3*d* and 4*f* ions and the magnetocaloric effect exhibited by these cluster-type systems.

- synthesis and magneto-structural characterization of some 3*d*-4*f*, $[M^{II}_6Ln^{III}_6]$, heterododecanuclear systems exhibiting slow relaxation of the magnetisation; such polynuclear systems are obtained by connecting six heterodinuclear units, $[M^{II}Ln^{III}]$, using oxalato bridges.

- synthesis and characterization of some tetranuclear complex systems, $[M^{II}{}_2Ln^{III}{}_2]$, (M^{II} = Co^{II} and Cu^{II}), with oxalato bridged heterobinuclear systems as a starting point and targeting their magnetic and magnetocaloric properties.

- synthesis of 3*d* and 3*d*-3*d*' systems respectively, using a selection of organic ligands, for the engineering of complex systems displaying magnetic properties and of Metal Organic Frameworks (MOF) type materials respectively.

Keywords: transitional metal, lanthanide, heteropolynuclear sistems, cluster, Single Molecule Magnet, Single Ion Magnet, Metal Organic Frameworks, magneto-structural correlations, nanomagnetic domain, magnetocaloric effect (MCE).

Contents

This thesis summarizes the results obtained during the three year research carried out on the synthesis, structural and magnetic characterization of a series of heteropolymetalic 3*d*-4*f* clusters exhibiting interesting magnetic properties such as slow magnetic relaxation and magnetocaloric behaviour. In the final section the structural and spectral investigation of some homopolynuclear 3*d*-3*d'* systems as precursors for magnetic materials are also discussed.

The thesis is divided into two main sections, the first one discussing the theoretical framework of molecular magnetism and recent advances in the field; the second section highlights the original contributions of the candidate. Fundamental theoretical notions pertaining to the field of molecular magnetism and being critical to the thorough understanding of the magnetization and slow magnetic relaxation processes are first introduced. These fundamental concepts form the foundation for the synthetic strategies employed for engineering monomolecular magnet type heterometalic 3*d*-4*f* systems.[1-5]

Further, a significant part of the first section is dedicated to the qualitative and quantitative treatment of the magnetocaloric effect (MCE). The most significant literature contributions reporting on the structure and magnetocaloric behaviour of molecular compounds containing 3*d*-4*f* coupled ions is also systematically reviewed

The candidate's original contribution starts by presenting the synthesis and magneto-structural characterization of some novel heteropolynuclear $[M^{II}_6Ln^{III}_6]$ systems synthesized using 3-formylsalicylic acid.[6-8]

The contents of chapter IV highlight the use of a novel strategy to synthesize heteropolynuclear 3*d*-4*f* systems with oxalato bridges, an otherwise unexplored topic in the chemistry of 3*d*-4*f* coordination compounds. The novelty of the proposed strategy relies on the use of oxalato bridges to connec six heterobinuclear $[M^{II}Ln^{III}]$ units into a heterododecanuclear cluster displaying interesting magnetic properties.

The magnetic and magnetocaloric properties exhibited by some novel tetranuclear coordination complexes containing $[Co^{II}Ln^{III}]$ and $[Cu^{II}Ln^{III}]$ fragments connected through oxalato bridges are investigated and reported in chapter V (i.e. the magnetic properties of [$Co^{II}_2Tb^{III}_2$] and the magnetocaloric behaviour of [$Cu^{II}_2Gd^{III}_2$]).

Finally, the last chapter is dedicated to a series of new 3*d*-3*d*' coordination compounds synthesized using three ligands: H_3L, the oxime of the 3-formylsalicylic acid; H_3felden, the *N,N,N*-dimethylenediamine(2,4,6-triformylfluoroglucinol) anion and (*S, R*) – valbn, the *N,N'*-binaphtylbi(3-methoxysalicylideneiminato) anion.

ORIGINAL CONTRIBUTIONS

Chapter III. The magnetocaloric effect in heterododecanuclear molecular systems

III.1. The synthetic strategy for dodecanuclear [$M^{II}_6Ln^{III}_6$] complexes, (M^{II} = Cu, Zn; Ln^{III} = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho)

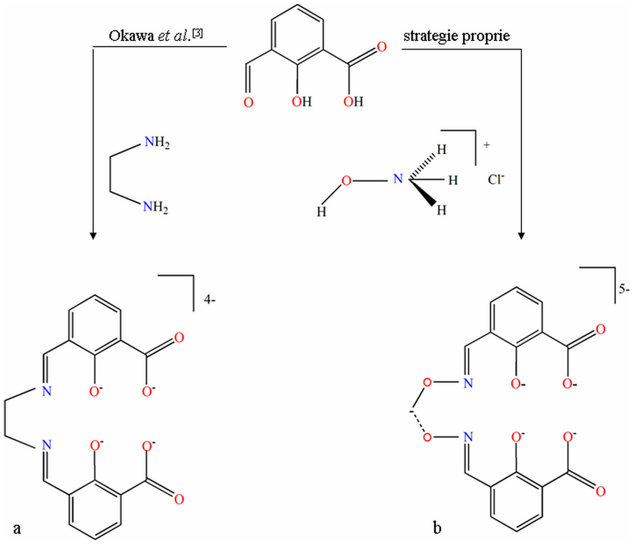
The rational design and synthesis of polynuclear systems in general and 3*d*-4*f* systems in particular requires the control over:

► the nuclearity (i.e. the number of metal ions)

► the dimensionality of the polymetalic system

► the metal centers' topology

Investigating the feasibility of synthesizing heterometallic 3d-4f systems with high nuclearity and exhibiting magnetic and magnetocaloric behaviour was the main goal of the research reported in this chapter. As a starting point, Okawa's[9] synthetic strategy was adapted by utilizing a Schiff base ligand, a derivative of 3-formylsalicylic acid, and the 3*d* (Cu^{II} şi Zn^{II}) and 4*f* (Ln^{III}) metal ions. This adaptation consists of replacing the ethylenediamine originally used by Okawa et al. with hydroxylamine in order to obtain an oxime with increased flexibility which, in the presence of the aforementioned metal ions, would lead to heteropolynuclear structures (**scheme III.1**).



Scheme.1. The synthesis of Okawa's ligand[3] (a) versus the modified approach employed to obtain a supramolecular bicompartimental ligand (b).

III.2. The characterization of $[M^{II}_6Ln^{III}_6]$ dodecanuclear systems (M^{II} = Cu, Zn; Ln^{III} = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho)

► $[Cu^{II}_6Ln^{III}_6]$

Dodecanuclear 3*d*-4*f* complexes were crystallized by slow evaporation of the solvent at room temperature and were characterized through single crystal X-ray diffraction. These measurements revealed the existence of a neutral dodecanuclear cluster containing six copper(II) ions and six lanthanide(III) ions. Compounds **1** – **9**, $[\{(HL)(L)(DMF)Cu^{II}Ln^{III}(DMF)(H_2O)\}_6]\cdot 6DMF$, Ln^{III} = Gd **1**, Tb **2**, Dy **3**, Ho **4**, Pr **5**, Nd **6**, Sm **7**, Eu **8**, La **9**; Ln^{III} = Gd **1**, Tb **2**, Dy **3**, Ho **4**, Pr **5**, Nd **6**, Sm **7**, Eu **8**, La **9**, are isostructural. The molecular structure of the dodecanuclear cluster containing Cu^{II} and Gd^{III} respectively is shown in **figure III.1**.

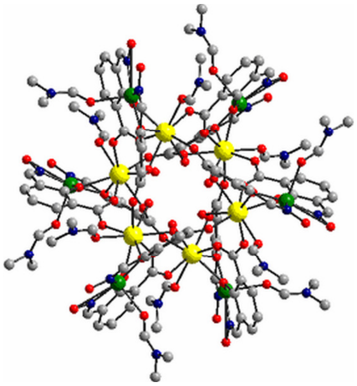


Figure III.1. The crystalline structure of the compund $[\{(HL)\text{-}L)(DMF)Cu^{II}Gd^{III}(DMF)(H_2O)\}_6]\cdot 6DMF$ **1**

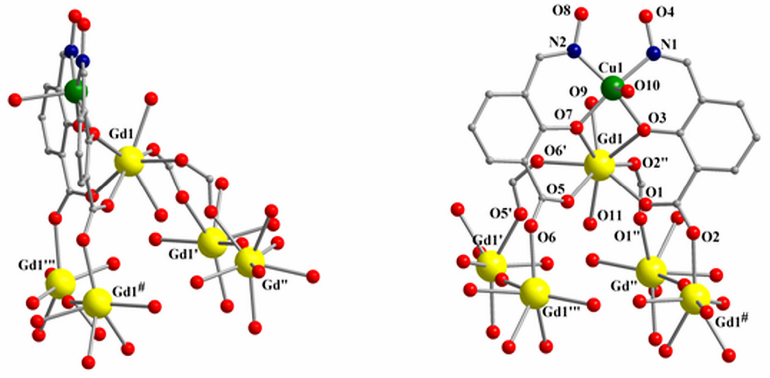
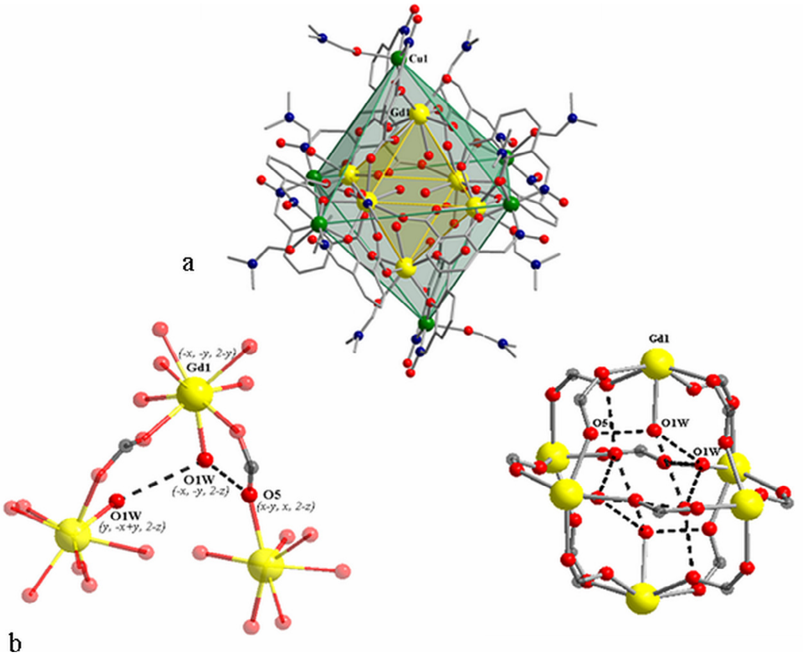


Figure III.2. *Syn-anti* connectivity between the Gd^{III} ions through carboxilato groups.

The dodecanuclear $[Cu^{II}_6Gd^{III}_6]$ complex is obtained by connecting six binuclear $[Cu^{II}Gd^{III}]$ units through carboxilate bridges: each carboxilato group is coordinated to two

Gd^{III} ions in a *syn-anti* manner (**figure III.2**), the Gd^{III} ions being each connected to four other identical ions through carboxilato groups. The interatomic distances between the gadolinium atoms are: Gd1···Gd1′ = 5.982, Gd1···Gd1″ = 6.075, Gd1···Gd1‴ = 5.982 and Gd1···Gd1$^{\#}$ = 6.075 Å (symmetry codes: ′: −x + y; −x; z. ″: y; −x + y; 2 − z. ‴: −y; x−y, z; #: x−y; x; 2 − z.).

Because joining together the 4*f* ions leads to the formation of an octahedron placed inside another octahedron formed by joining together the Cu^{II} ions, this newly obtained structure can be described as being a 3*d*-4*f* cluster with an “octahedron inside an octahedron” structural motif (**figure III.3a**).



FigureIII.3. ”Octahedron in an octahedron” structure and a detail of the hydrogen bond system present in compound **1.**

In compound **1**, within the “octahedron in an octahedron” structure, the gadolinium(III) ions, in a square antiprism surrounding, each contain in their coordination sphere a water molecule. As illustrated in **figure III.3b**, this structural motif obtained by connecting identical ions highlights the formation of a network of hydrogen bonds, each water molecule generating two hydrogen bonds (O1W – O1W”’ = 2.975 and O1W – O5” = 2.647 Å, with the symmetry codes: ″: y; –x + y; 2 – z. ‴: –y; x–y, z): one of them formed with the oxygen atom belonging to the water molecule coordinated to a neighbouring Gd^{III} ion and the other formed with an oxygen atom belonging to the carboxilate anion.

► $[Zn^{II}_6Ln^{III}_6]$

The reason for choosing the Zn^{II} and Ln^{III} ions is determining the magnetic contribution of the 4*f* metallic centers within the dodecanuclear $[M^{II}_6Ln^{III}_6]$. The zinc(II) ion is a diamagnetic specie with a d^{10} electronic configuration. Consequently, the sole contribution to the overall magnetic behavior will belong to the lanthanide ion. The presence of lanthanide ions can also lead to liuminescent properties of the compund, the antenna effect resulting from the coordination of the zinc(II) ion.

The dodecanuclear 3*d*-4*f* complexes containing zinc(II) and lanthanide(III) ions were obtained as single crystalls, the crystallographic measurements revealing the existence of a neutral dodecanuclear cluster (**figure III.4**) containing six zinc and six lanthanide ions. Compounds **10** and **11**, $[\{(HL)(L)(DMF)Zn^{II}Ln^{III}(DMF)(H_2O)\}_6]\cdot 3DMF\cdot 4.2H_2O$, Ln^{III} = Dy **10**, Sm **11**, are isostructural with those containing copper(II) and lanthanide(III) ions.

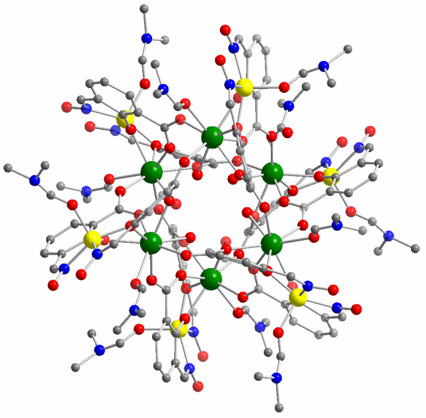


Figure III.4. Molecular structure of the compound $(HL)(L)(DMF)Zn^{II}Dy^{III}(DMF)(H_2O)\}_6]\cdot 3DMF\cdot 4.2H_2O$ **10.**

III.3. Magnetic and magnetocaloric properties of $[M^{II}_6Ln^{III}_6]$ clusters

III.3.1. Magnetic characterization of the $[Cu^{II}_6Gd^{III}_6]$ complex

The graphical representation of the product $\chi_M T$ versus temperature serves to highlight the magnetic behaviour of compound **1** (**figure III.5**), where χ_M is the molar magnetic susceptibility.

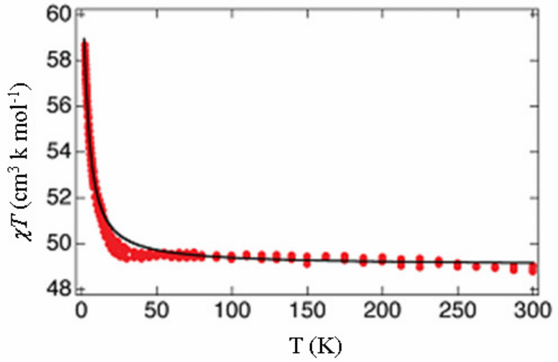


Figure III.5. The variation of the $\chi_M T$ product versus temperature for compound **1** (●), and the continuous line representing a fit of the experimental data (-).

At 300 K, the product $\chi_M T$ has a value of 49.5 cm^{3}kmol^{-1} slightly higher than the value obtained theorectically (49 cm^3 k mol^{-1}) and taking into account 12 spin carriers, six copper(II) and six gadolinium(III) magnetically non-interacting ions. The [Cu$^{II}_6$Gd$^{III}_6$] system **1** can be regarded as comprising six independent [Cu^{II}Gd^{III}] magnetic entities, each one characterized by a $S = 4$ ground state. The ferromagnetic interaction within each of the six heterobinuclear fragments is also confirmed by the variation in the system's **1** magnetization as a function of magnetic field (**figure III.6**), in the range 0 – 7 T, and temperature range of 20 – 2.3 K.

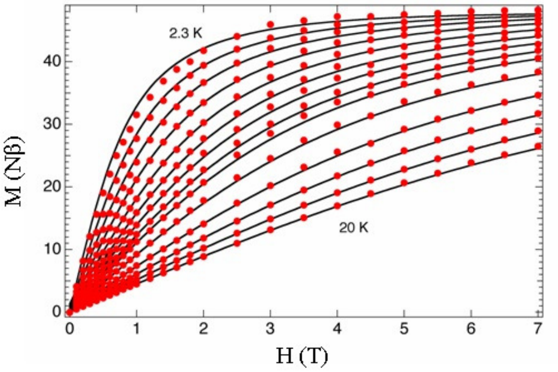


Figure III.6. Relationship between magnetization and magnetic field intensity in compound **1** (●), where the continuous line (-) is the Brillouin function for six uncoupled units (S = 4).

The dodecanuclear cluster **1** , has all the necessary characteristics to exhibit a significant magnetocaloric effect (**figure III.7**): Gd^{III} ion isotropy, weak the ferromagnetic interaction and high metal/ligand mass ratio.[16]

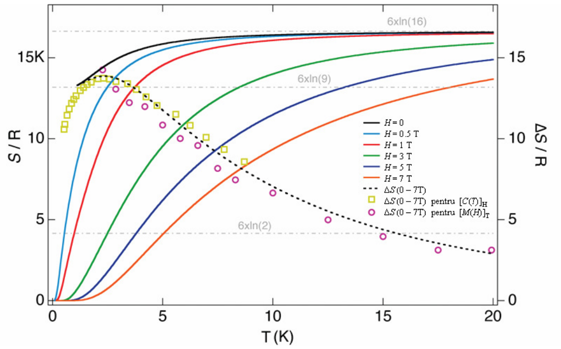


Figure III.7. S/*R* entropy versus *T* curve obtained at different magnetic field values, *H*, (continuous line). The entropy variation ΔS_m for $\Delta H = 0 - 7$ T; $\Delta S_m[0 - 7$ T$]$ estimated from the specific heat and magnetization data using Maxwell's equations (dashed line).

The maximum entropy variation $\Delta S_m(T)$ [0 – 7 T] = 13.8*R* (molar units) or $\Delta S_m(T)$ [0 – 7 T] = 23.5 J Kg^{-1} K^{-1}(mass units) was estimated at a temperature of 2.3 K.

III.3.2. Magnetic characterization of the $[Zn^{II}_6Dy^{III}_6]$ complex

Magnetic characterization of the compund $[Zn^{II}_6Dy^{III}_6]\cdot$**10** was carried out in continuous (DC), **figure III.8**, and alternating magnetic fields (AC) respectively, **figure III.9**.

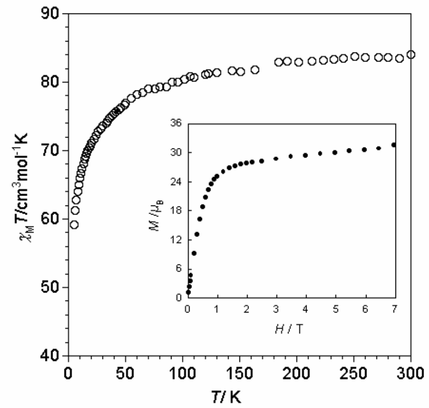


Figure III.8. The product $\chi_M T$ versus temperature for compound **10** under a 5000 G direct current magnetic field ($300 \leq T \leq 30$ K) and 250 G ($T < 30$ K) respectively. Inset shows the magnetization versus *H* at 2.0.

The dynamic magnetic measurements (AC) at frequencies in the range 0 – 1000 Hz have revealed the existence of magnetic signals corresponding to both the real (χ_M') and the imaginary (χ_M'') components of the magnetic susceptibility as shown in **figure III.9**.

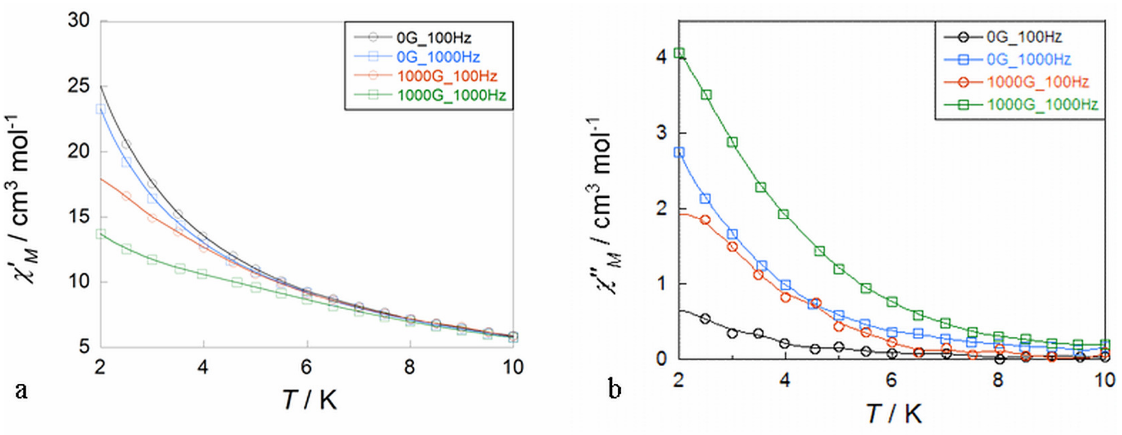


Figure III.9. The relationship between χ_M' (a) and χ_M'' (b) respectively and *T* in AC for compound **10.**

The dodecanuclear system [$Zn^{II}_6Dy^{III}_6$] **10**, exhibiting a single ion magnet behaviour, is in fact a summation of six dysprosium(III) based monomolecular nanomagnets.

Chapter IV. Molecular heterododecanuclear 3*d*-4*f* systems with single molecule magnet behaviour

The goal of the research presented in chapter IV was to develop novel synthetic routes toward discrete polymetallic 3*d*-4*f* systems characterized by high nuclearity. The proposed strategy si based on connecting oligonuclear 3*d*-4*f* cationic complexes through the oxalato ligand. The synthesis of such 3*d*-4*f* oxalato-bridged heteropolymetallic systems is not a trivial task since a direct reaction between the 3*d*, 4*f* ions and oxalato anion will only result in amorphous compounds. So far, only a few homometallic oxalate-bridged coordinations polymers have been obtained usig ascorbic acid as a source of oxalate ligands. .[10-13]

IV.1. Structural characterization of dodecanuclear [$M^{II}_6Ln^{III}_6$] complexes

Three families of dodecanuclear 3*d*-4*f* clusters were obtained by applying the above-mentioned strategy, i.e. by connecting heterodinuclear entities through oxalato bridges. Crystallographic analysis via single crystal X-ray diffraction of the three families of compounds, [$Cu^{II}_6Ln^{III}_6$], [$Ni^{II}_6Ln^{III}_6$], [$Zn^{II}_6Ln^{III}_6$], confirms that they share the same structural motif.

► [$\mathrm{Cu^{II}_6Ln^{III}_6}$]

Single crystal X-ray diffraction measurements revealed the existence of a dodecanuclear cluster comprising six copper(II) and six lanthanide(III) ions: $[\{\mathrm{Cu^{II}(valpn)Ln^{III}(CH_3COO)_2}\}_6(\mathrm{C_2O_4})_6]\cdot 3\mathrm{H_2O}$, $\mathrm{Ln^{III}}$ = Dy **12**, Tb **13**, **figure IV.1**. Additionally, it can be seen that the lanthanide ions are connected by bis-chelating ligands.

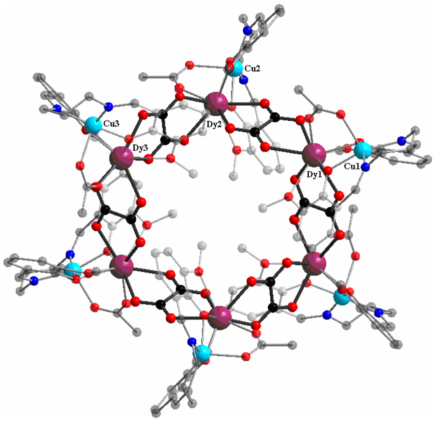


Figure IV.10. Molecular structure of [$\mathrm{Cu^{II}_6Dy^{III}_6}$] **12**.

The asymmetric unit of the heterododecanuclear copper(II) and dysprosium(III) system is depicted in **figure IV.2**. The oxalate anions function as a bridge between two 4*f* ions, the oxalate group coordinating in bis(chelate μ_1-η^2) mode. The acetate anion acts as a bridge between the 3*d* and 4*f* ions of the same heterodinuclear unit, the acetate group coordinating a μ_2 *syn* – *syn* bridge.

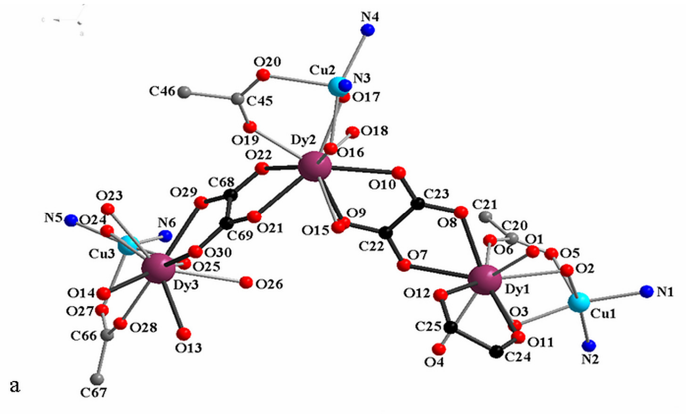


Figure IV.11. The asymmetric unit of the dodecanuclear complex **12**.

The lantahanide ions connected through oxalato bridges are arranged in a chair like conformation (**figure IV.3**).

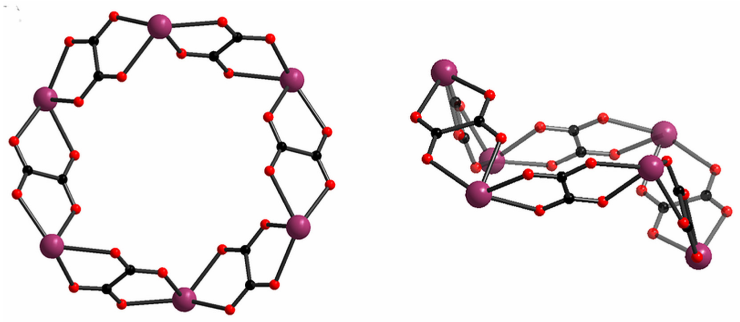


Figure IV.12. Chair conformation of the dodecanuclear compound **12.**

► $[Ni^{II}_6Ln^{III}_6]$

The structure of the heterododecanuclear compound, $[\{Ni^{II}(valpn)Ln^{III}(HCOO)_{0.6}(NO_3)_{0.4}(H_2O)_{0.33}(EtOH)_{0.67}\}_6(C_2O_4)_6]\cdot xSolv$ **14**, **figure IV.4**, consists of similar six binuclear units being connected together through oxalato ligands.

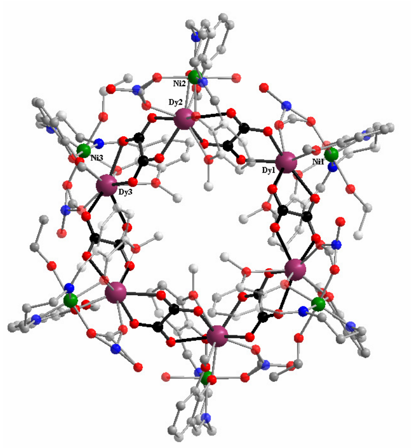


Figure IV.13. Molecular structure of $[Ni^{II}_6Dy^{III}_6]$ **14**.

From the crystalline structure of the dodecanuclear compound one can observe that the heterobinuclear units are connected through oxalate anions while the different ions pertaining to one heterodinuclear $[M^{II}Ln^{III}]$ unit are separated by formiato and nitrato bridges respectively, characterized by a certain occupancy degree. The coordination manner of the nitrate and formiate groups respectively is μ_2 *syn – syn,* while that of the oxalate groups is of the bis(chelate μ_1-η^2).

► $[Zn^{II}_6Ln^{III}_6]$

The structure of compounds $[\{Zn^{II}(valpn)Dy^{III}(HCOO)_{0.78}(NO_3)_{0.22}\}_6(C_2O_4)_6]\cdot 2.5DMF\cdot 2CH_3OH\cdot 2.5H_2O$ **15**,
$[\{Zn^{II}(valpn)Tb^{III}(HCOO)_{0.77}(NO_3)_{0.23}\}_6(C_2O_4)_6]\cdot 1.5DMF\cdot 1CH_3OH\cdot 9H_2O$ **16**,
$[\{Zn^{II}(valpn)Sm^{III}(CH_3COO)\}_6(C_2O_4)_6]\cdot 1DMF\cdot 2CH_3CH_2OH\cdot 2H_2O$ **17**,
$[\{Zn^{II}(valpn)Eu^{III}(CH_3COO)\}_6(C_2O_4)_6]\cdot 5H_2O$ **18**,
$[\{Zn^{II}(valpn)Er^{III}(CH_3COO)\}_6(C_2O_4)_6]\cdot 5H_2O$ **19** comprises zinc(II) and lanthanide(III) ions and is the result of connecting, through oxalato bridges, six identical heterobinuclear units.

The dodecanuclear $[Zn^{II}_6Ln^{III}_6]$ compounds are isostructural, the difference between the members of this family residing in the connecting bridge (formiate and nitrate anions for compounds **15** and **16**; acetate anions for compounds **17** – **19**) connecting the ions 3*d* and 4*f* belonging to the same heterodinuclear unit and also the crystallization solvent molecules. The crystall structure of the heterododecanuclear Zn^{II} and Dy^{III} compound, **15**, is depicted in **figure IV.5**.

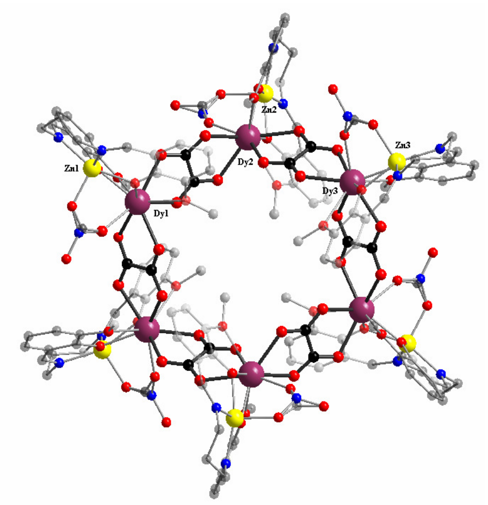


Figure IV.14. The crystal structure of $[Zn^{II}_6Dy^{III}_6]$ **15**.

IV.2. Magnetic and fluorescence properties of the $[M^{II}_6Ln^{III}_6]$ complex

IV.2.1. Slow magnetic relaxation in dodecanuclear $[Cu^{II}_6Tb^{III}_6]$, $[Zn^{II}_6Dy^{III}_6]$ and $[Ni^{II}_6Dy^{III}_6]$ systems

► $[Cu^{II}_6Tb^{III}_6]$

Magnetic susceptibility measurements were carried out in both (DC) and (AC) modes. AC measurements (**figure IV.6**) were recorded in the temperature range 2 – 6 K, a field intensity of 1500 G and a frequency range of 8000 – 100 Hz.

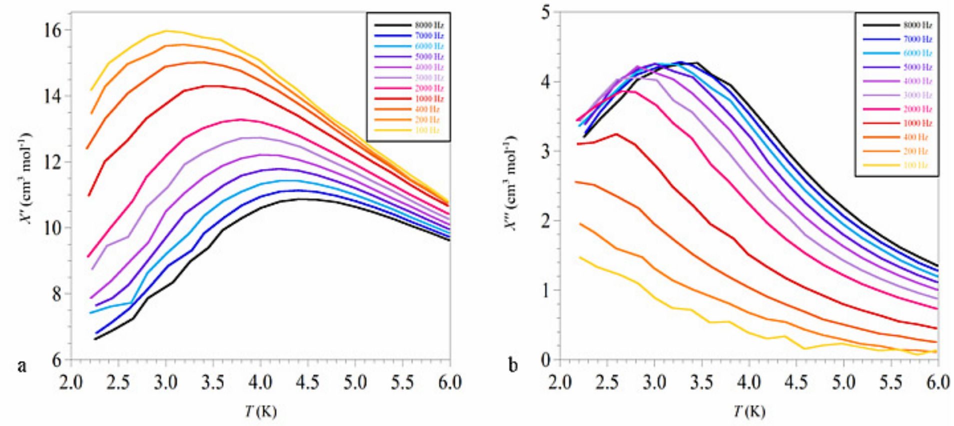


Figure IV.15. χ'_M versus T (a) and χ''_M versus T (b) curve for the $[Cu^{II}_6Tb^{III}_6]$ complex.

This magnetic study was complemented by the dynamic characterizationon of the compound using Arrhenius'. From the linear fitting of the magnetic data (**figure IV.7**) one can derive both the magnitude of the energy barrier (12.12 cm^{-1}) and the pre-exponential factor τ_0 ($5.91 \cdot 10^{-8}$ s).

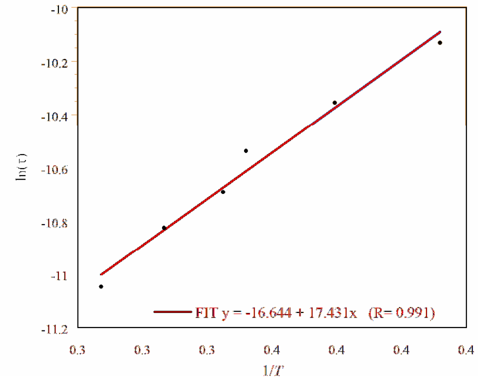


Figure IV.16. Ln(τ) versus $1/T$ at 1500 G (linear fit represented by the solid line).

► $[Ni^{II}_6Dy^{III}_6]$

Magnetic measurements were carried out in both continuous (DC) and alternating (AC) modes. Magnetic susceptibility was recorded in AC in the temperature range 2 – 7 K, a field intensity of 2500 G and frequency range of 10000 – 600 Hz. The Ni^{II} and Dy^{III} complex exhibits a magnetic signal for both the real and imaginary components of the magnetic syusceptibility (χ'_M and χ''_M respectively) as seen in **figure IV.8**, this being indicative of a SMM type behaviour.

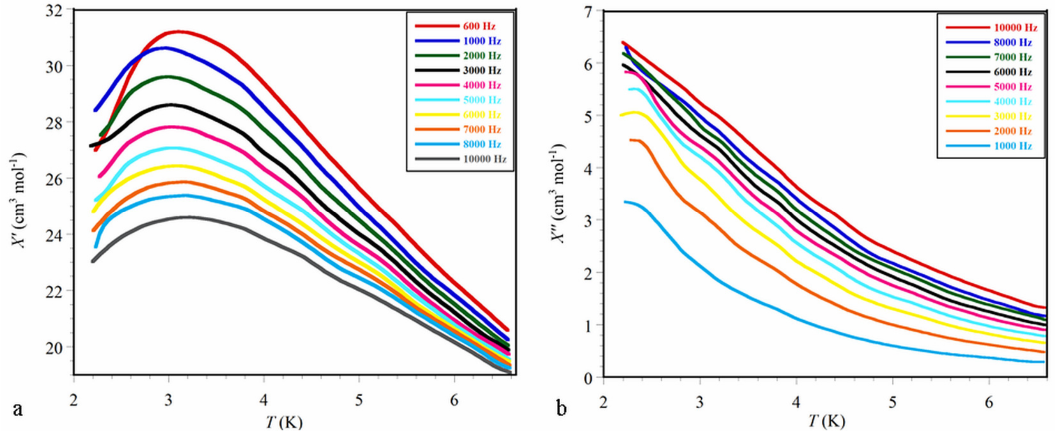


Figure IV.17. χ'_M versus T (a) and χ''_M versus T (b) curves for the $[Ni^{II}_6Dy^{III}_6]$ cluster.

Because the curve χ''_M versus T reaches maximum at a temperature lower than 2 K the magnitude of the energy barrier E_a and the value of the pre-exponential factor were calculated using Bartolomé's method[17]. Thus, after representing graphically $\ln(\chi_M''/\chi_M')$ versus $1/T$ the values +7.75 cm^{-1} for the energy barrier and $2.20 \cdot 10^{-7}$ s for the pre-exponential factor (τ_0) are extracted (**figure IV.9**).

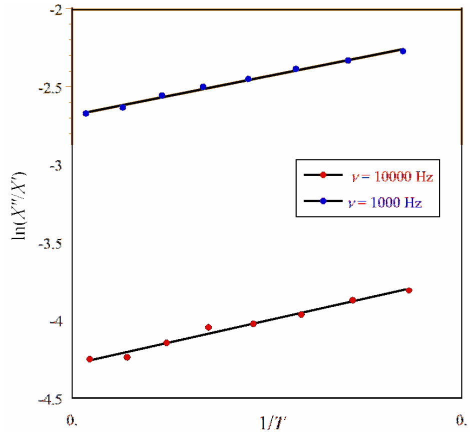


Figure IV.18. $\ln(\chi_M''/\chi_M')$ versus $1/T$ for a DC magnetic field intensity of 100 G and an AC field intensity of 2500 G and two frequencies (1000 and 10000 Hz respectively).

The dodecanuclear [$\mathrm{Ni^{II}}_6\mathrm{Dy^{III}}_6$] cluster comprises six SMM type units, each heterobinuclear unit exhibiting a SMM behaviour.

► [$\mathrm{Zn^{II}}_6\mathrm{Dy^{III}}_6$]

Slow relaxation of the magnetizations static and dynamic magnetic measurement were performed and AC magnetic susceptibility was recorded in a temperature range of 2 – 10 K in a magnetic field intensity of 1000 G and frequency in the range of 1400 – 350 Hz. The dodecanuclear system comprising $\mathrm{Zn^{II}}$ and $\mathrm{Dy^{III}}$ exhibits signals for both the real and imaginary component of the magnetic susceptibility (χ'_M and χ'_M respectively), the curves in **figure IV.10** suggesting a SIM type behaviour.

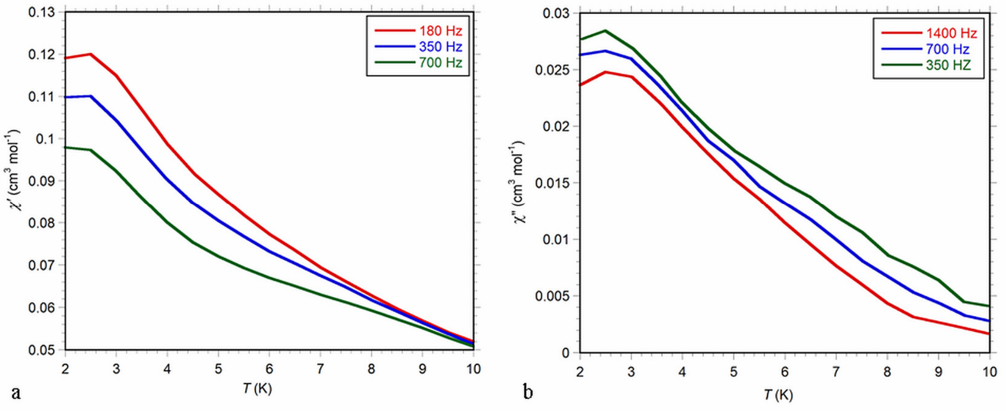


Figure IV.19. χ'_M versus T (a) and χ''_M versus T (b) curves recorded for the [$\mathrm{Zn^{II}}_6\mathrm{Dy^{III}}_6$] cluster.

Magnetig data fitting depicted in **figure IV.11** results in a magnitude of the energy barrier E_a of 2.09 cm^{-1} and a value of the pre-exponential factor τ_0 of $3.09 \cdot 10^{-3}$ s.

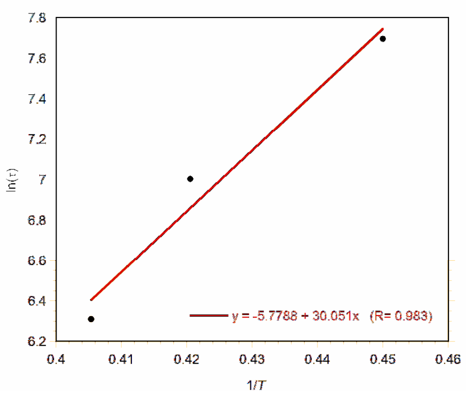


Figure IV.20. ln(τ) versus 1/T in a magnetic field intensity of 1000 G (continuous line represents the fit line).

The dodecanuclear $[Zn^{II}_6Dy^{III}_6]$ cluster comprises six SIM (Single Ion Magnet) type units, each dysprosium(III) ion displaying a monomolecular magnet behaviour.

IV.5.2. Luminescent properties of the dodecanuclear $[Zn^{II}_6Ln^{III}_6]$ systems

Luminescence spectra were recorded for the heterododecanuclear $[Zn^{II}_6Ln^{III}_6]$, Ln^{III} = Tb **16**, Sm **17** si Eu **18** systems and excitation was achieved using λ_{ex}= 370 nm (**figure IV.12a**). The emission is recorded in the visible range: λ_{em}= 597 nm for the Sm^{III} complex, 617 nm for the Eu^{III} complex and finally 543 nm for the Tb^{III} complex.

The measured fluorescence life times (**figure IV.12b**) for compounds **16**, **17** and **18** respectively were: 330, 7 and 131 μs respectively.

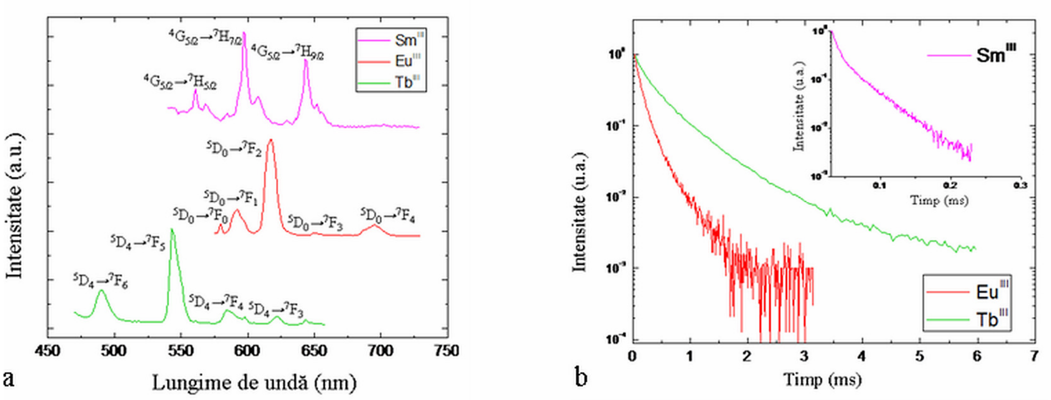


Figure IV.21. Photoluminescence spectra for compounds **16**, **17** and **18** respectively measured on powders at room temperature (λ_{ex}= 370 nm; λ_{em}= 597 nm for Sm^{III}, 617 nm for Eu^{III} and 543 nm for Tb^{III}).

Chapter V. Slow magnetic relaxation and magnetocaloric behaviour in heterotetranuclear 3*d*-4*f* complexes

Using the same synthetic approach described previously for obtaining dodecanuclear $[M^{II}_6Ln^{II}_6]$ systems with oxalato bridges, a series of novel tetranuclear $[M^{II}_2Ln^{II}_2]$, $[M^{II}$ = Cu^{II}, $Co^{II}]$ compounds was obtained starting from the following building blocks:

- bicompartimental Schiff base ligand ($valpn^{2-}$ = obtained via condensation of an *o*-vaniline and 1,3-diaminopropane) such as to accommodate simultaneously 3*d* and 4*f* metallic ions.

- 3*d* and 4*f* metallic ions.
- oxalate, formiate and acetate anions resulting from the slow decomposition of the ascorbic acid.

V.1. Structural characterization of the tertranuclear [$M^{II}_2Ln^{III}_2$] systems

The structure of the newly synthesized compounds comprises two different tetranuclear [$M^{II}_2Ln^{III}_2$] units. The backbone of a tetranuclear unit consisits of two heterodinuclear [$M^{II}Ln^{III}$] entities connected through oxalato bridges. The [$M^{II}_2Ln^{III}_2$] fragments containing cobalt(II) ions and different lanthanide(III) species exhibit a structural model similar to that of the copper(II) and gadolinium(III) containing complexes.

► [$Cu^{II}_2Gd^{III}_2$]

The tertranuclear 3*d*-4*f* complex, [$Cu^{II}_2Gd^{III}_2$] (**figure V.1**), was characterized using single crystal X-ray diffraction. The crystallographic measurement have pointed out the existence of two tetranuclear units, each one containing two copper(II) ions and two lanthanide(III) ions.

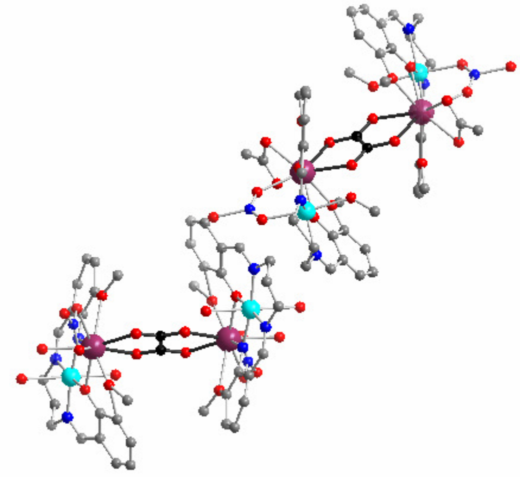


Figure V.1. Molecular structure of the tetranuclear copper(II) and gadolinium(III) compound, **20**.

The complex heteronuclear **20** system consists of two different tetranuclear [$Cu^{II}_2Gd^{III}_2$] units, henceforth labeled “tetranuclear unit 1” and “tetranuclear unit 2”. The difference between the two tetranuclear units lies with the donor atoms in the coordination sphere of the copper(II) and gadolinium(III) ion respectively.

► $[Co^{II}_2Ln^{III}_2]$

The tetranuclear 3*d*-4*f* complexex, $[Co^{II}_2Ln^{III}_2]$, (Ln^{III} = Gd, Tb), were obtained as single cristal through slow tube diffusion and were structurally characterized via X-ray diffraction. Crystallographic measurements have indicated that two tetranuclear units each containing two cobalt(II) and two lanthanide(III) ions are formed. Only the $[Co^{II}_2Gd^{III}_2]$ **21** compound will be treated in detail **(figure V.2.**). The heterotetranuclear $[Co^{II}_2Tb^{III}_2]$ **22** has a sytructural model similar to that of the Co^{II} - Gd^{III} compound. The difference between the two tetranuclear entities, present in the coordination sphere of the $[Co^{II}_2Gd^{III}_2]$ compound are replaced by nitrate groups in the $[Co^{II}_2Tb^{III}_2]$ compound.

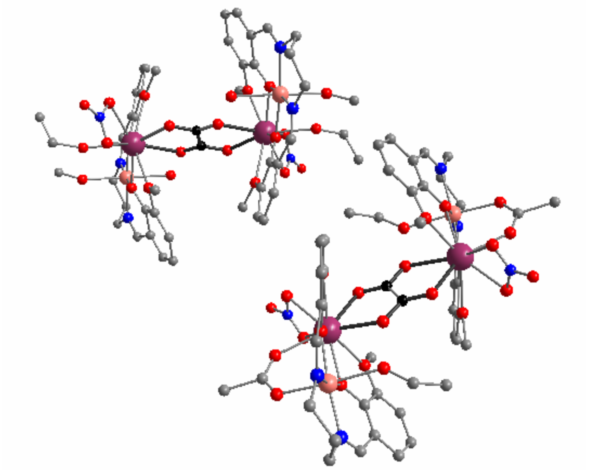


Figure V.2. Molecular structure of the tetranuclear cobalt(II) and gadolinium(III) compound.

V.2. Magnetic $[Co^{II}_2Tb^{III}_2]$ and magnetocaloric $[Cu^{II}_2Gd^{III}_2]$ properties in tertranuclear complexes

A novel family of complexes containing cobalt(II) and lanthanide(III) ions is reported in the second part of the fifth chapter and the magnetic properties of a member of this family, $[Co^{II}_2Tb^{II}_2]$ **22**, are discussed.

A copper(II) and gadolinium(III) compound reported herein was also analyzed and it was found that it elicits a magnetocaloric behaviour. The intrinsic characteristics of the paramagnetic centers belonging to these heteropolynuclear systems are of major importance:

- the copper(II) ion: paramagnetic species (1 unpaired electron) with a d^9 electronic configuration and ½ spin value.

- the cobalt(II) ion: paramagnetic specie (3 unpaired electrons) with a d^7 elevctronic configuration 3/2 spin value. Due to the presence of a high magnetic anisotropy arising from a significant spin orbit coupling the paramagnetic cobalt(II) ion is an important source of molecular magnets.

- the lanthanide(III) ions: Tb^{III} and Gd^{III} respectively are paramagnetic species with an f^8 electronic configuration (the ground state term is $^7F_6$) and f^7 electronic configuration (the ground state term is $^8S_{7/2}$).

► $[Cu^{II}{}_2Gd^{III}{}_2]$

The tetranuclear copper(II) and gadolinium(III) complex was subjected to measurements aimed at determining the magnitude of its magnetocaloric behaviour. To emphasize the cooling properties of the complex, its specific heat versus temperature curve was recorded in the temperature range 0.3 – 15 K (**figure V.3.**).

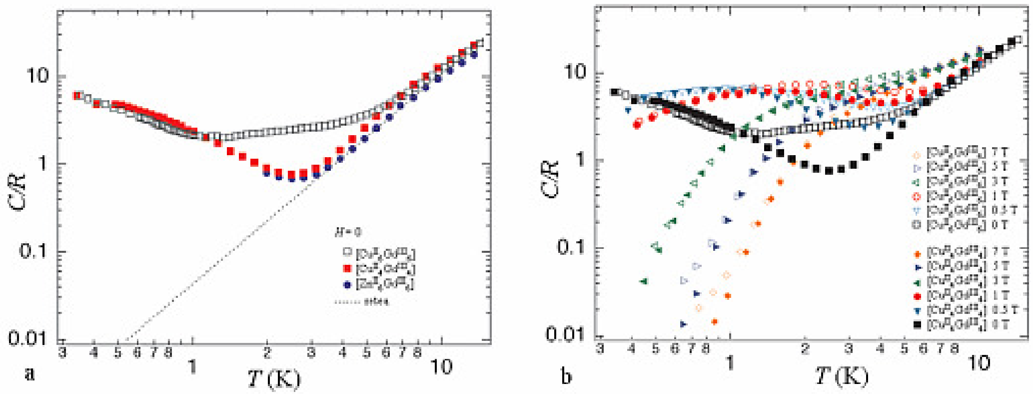


Figure V.3. The variation of specific heat with temperature at zero magnetic field intensity for the three systems containing 3*d* and 4*f* ions respectively (a). Specific heat versus temperature curve in a magnetic field of intensity in the range 7 – 0 T for compounds **1** and **20** (b).

By comparing the magnetic behaviour of the $[Cu^{II}_6Gd^{III}_6]$ **1** complex described previously in chapter III with that of systems containing oxalate bridges (compound **20** and the dodecanuclear Zn^{II} and Gd^{III} compound respectively) one can readily notice a significant similitude in terms of specific heat, the only notable difference residing in the decrease of the *C*/*R* value in the temperature range 2-3 K. For temperatures below 2 K the three systems behave in a similar fashion (**figure V.3a**). The graphical representation of the specific heat versus temperature curve (at magnetic field values of 0, 0.5, 1, 3, 5 şi 7 T respectively) yields additional proof of the significand degree of similarity, especially in terms of magnetic behaviour, between the systems containing Cu^{II} and Gd^{III} ions (**figure V.3b**).

The computed value for the entropy variation for compound **20** using the same formula, i.e. $\Delta S_m = nR \ln(2S + 1)$, is notably close (23.0 J Kg^{-1} K^{-1}) to that of complex **1**, 23.5 J Kg^{-1} K^{-1}.

► $[Co^{II}_2Tb^{III}_2]$

In order to suppress the tunneling effect in the presence of static field, magnetic susceptibility measurements were carried out in an alternating current. The magnetic susceptibility determination was carried out for a temperature range of 2 – 12 K and by applying a magnetic field with an intensity of 1000 G and frequencies in the range of 10000 – 2000 Hz.

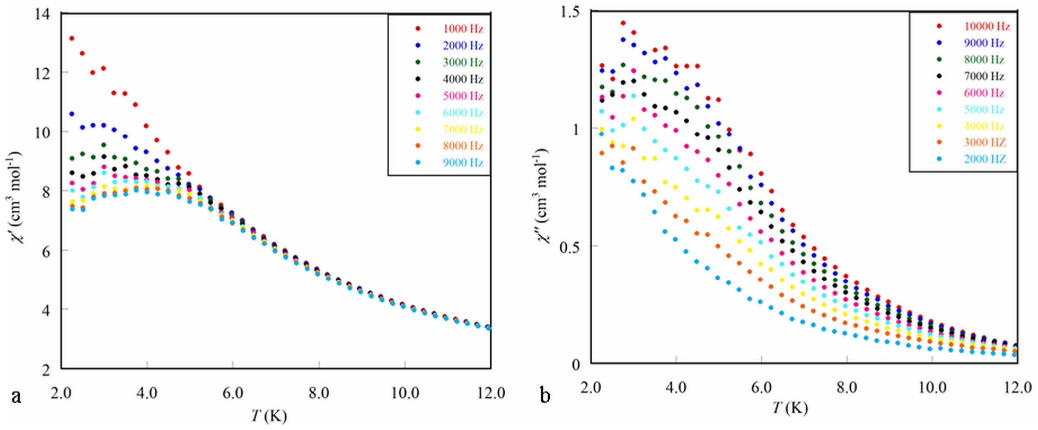


Figure V.4. χ'_M versus *T* (a) and χ''_M versus *T* (b) curves for compound **22**.

The Co^{II} and Tb^{III} complex exhibits a signal for both the dissipative (χ'_M) and the absorptive (χ''_M) component of the susceptibility (**figure V.4**) this being indicative of a SMM behaviour.

By applying Bartolomé's method and graphically representing $\ln(\chi''_M / \chi'_M)$ as a function of $1/T$ at two frequencies (**figure V.5**) one can extract an approximate value of the energy barrier (9.21 cm^{-1}) and the magnetization pre-exponential parameter ($9.22 \cdot 10^{-7}$ s).

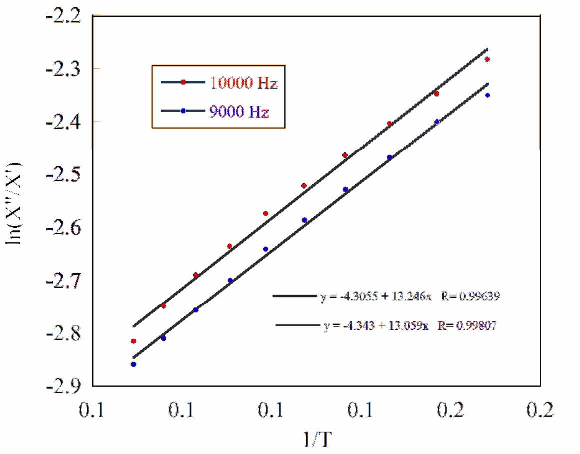


Figure V.5. The natural logarithm of the ratio χ_M''/χ_M' versus $1/T$ after applying a DC magnetic field with an intensity of 2500 G and an oscillating field with an intensity of 1000 G, at two different frequencies.

Chapter VI. Various homopolynuclear 3*d*-3*d* şi 3*d*-3*d*' systems

Structural ans spectroscopic characterization of some various 3*d*-3*d* şi 3*d*-3*d*' polynuclear complexes are discussed in the last chapter. These were engineered using three different ligands: H_3L – the oxime of the 3-formylsalicylic acid, (*S,R*)-H_2valbn - a Schiff base of *o*-vaniline and H_3felden – a Schiff base of 2,4,6-triformylfluoroglucinol) cupru(II), manganese(II) and manganese(III) transitional metal ions.

I. The compartimental H_3L ligand obtained via condensation of 3-formylsalicyclic acid and hydroxylamine.[14]

The synthetic strategy was aimed at obtaining heteropolynuclear 3*d*-3*d'* units containing Cu^{II} and Mn^{II} ions resembling the dodecanuclear compounds reported previously in chapter III. Bidimensional structures comprising homobinuclear Cu^{II} units connected together through hexacoordinated Mn^{II} ions were the result of the complexation reaction of the ligand (which had previously been deprotonated with a strong base) with a copper(II) and manganese(II) salt respectively.

II. The H_3felden ligand is a Schiff base resulting from the condensation of 2,4,6-triformylfluoroglucinol and 2,2-dimethyletilendiamine.[15-18] The synthetic goal was to obtain *Metal Organic Framework* (MOF) systems starting from the same H_3felden ligand. The rational design and synthesis of "honeycomb" networks with tunable porosity determined by the nature of the *spacer* was envisaged.

III. The compartimental blocking ligand (*S*,*R*) – H_2valbn obtained in a condensation reaction between *o*-vaniline and the (*S*) and (*R*) enantiomers of 1,1-binaftyl-2,2-diamine respectively was employed.[19-21] Using chiral ligands, i.e. (*S*,*R*) – H_2valbn, along with manganese(II) ions is aimed at studying the influence of chirality on the magnetic behaviour of the resulting coordination compounds.

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Publications list

Journal papers

1. *Dodecanuclear [$Cu^{II}_6Gd^{III}_6$] Nanoclusters as Magnetic Refrigerants*,
   Alina S. Dinca, Alberto Ghirri, Augustin M. Madalan, Marco Affronte, Marius Andruh, *Inorganic Chemistry*, **2012**, *51*(*7*), 3935–3937.

2. *Synthesis, crystal structure and magnetic properties of a new [$Zn^{II}_6Dy^{III}_6$] dodecanuclear motif*
   Alina S. Dinca, Julia Vallejo, Sergiu Shova, Francesc Lloret, Miguel Julve, Marius Andruh, *Polyhedron*, **2013**, *in press.*

Communications (oral and poster presentations)

1. ” Oligonuclear complexes as tectons in crystal engineering”
Alina-Simona Dinca, Marius Andruh
“Scientific Communications Session” Faculty of Chemistry of Bucharest, Bucharest, Romania / 13th May 2012 / presentation.

2. *Dodecanuclear [$Cu^{II}_6Gd^{III}_6$] Nanoclusters as Magnetic Refrigerants*
Alina-Simona Dinca, Alberto Ghirri, Augustin M. Madalan, Marco Affronte, Marius Andruh
“New Trends in Materials Science”Workshop, ID: POSDRU/89/1.5/S/58852, Romanian Academy, Bucharest, Romania / poster.

3. *Dodecanuclear [$Cu_6^{II}Ln_6^{III}$] nanoclusters (Ln = Gd, Tb, Dy, Ho). A new magnetic refrigerant*
Alina-Simona Dinca, Alberto Ghirri, Augustin M. Madalan, Marco Affronte, Francesc Lloret, Miguel Julve, Marius Andruh,
“The 40th International Conference on Coordination Chemistry (ICCC40)” Valencia, Spain, 09th-13th september 2012 / poster.

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