PNI-II-RU-PD-2012-3-0177

Photo-switchable heterometallic complexes. Toward light-controlled Single-Molecule and Single-Chain Magnet behavior

01.05.2013 – 31.10.2015

Director de proiect: Dr. Maria-Gabriela Alexandru

Mentor: Acad. Marius Andruh

Main objectives

- **Design and synthesis of new photo-switchable heterometallic complexes**. Assessment of photo-responsive potential

- **The achievement of light-induced nanomagnetic behavior**, with higher blocking temperature (than reported) using previously synthesized photo-active heterobimetallic and heterotrimetallic complexes.

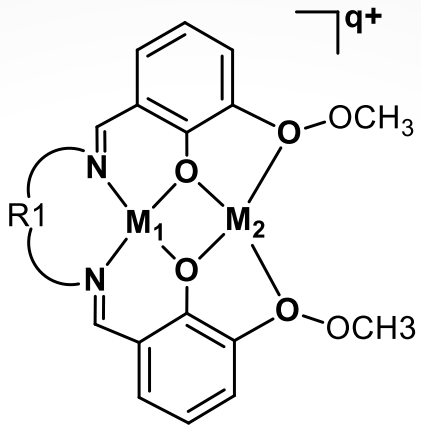
- **Magneto-structural correlations**. For a better understanding of the magnetic behavior it is important to identify the structural features that influence the spin exchange interactions. Discrete heterobimetallic complexes are useful as model compounds in order to develop efficient photo-switchable molecular materials.

Methodology

Task	Year		
	2013	2014	2015
1			
2			
3			
4			
5, 6			
P			

1. **Synthesis and crystallo-genesis** of coordination compounds
2. **Preliminary analysis** of the obtained complexes by means of FTIR, NIR-UV-Vis and elemental analysis
3. **Structural studies** through X-ray diffraction on single-crystal and on powder
4. **Magnetic measurements**: Preliminary DC magnetic measurements on SQUID magnetometer in the temperature range of 2 - 300 K; AC magnetic measurements on SQUID magnetometer to identify frequency dependence of in-phase (χ') and out-of-phase (χ'') magnetic susceptibility
5. **Photomagnetic measurements** on SQUID magnetometer at 5K by irradiating with UV light, in order to establish the photoresponsive properties of the obtained compounds
6. **RES and XPS** spectroscopy measurements

Synthetic strategy

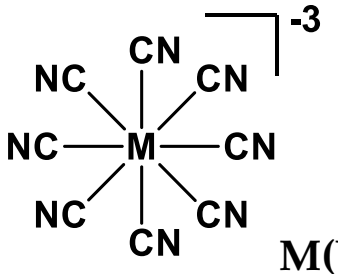


M1 = 3d metal ion

M2 = 3d or 4f metal ion

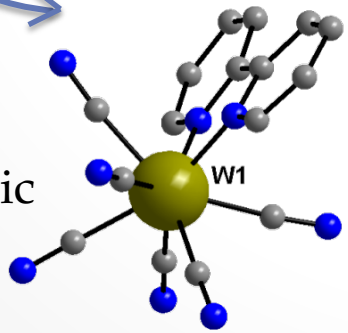
Node and spacer approach ⟶ **heterometallic complexes**

Homoleptic

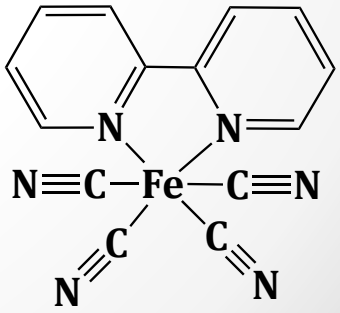


M(V) = Mo, W

Heteroleptic



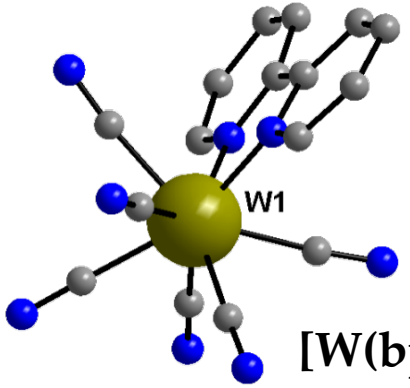
$[W(bpy)(CN)_6]^-$



$[Fe(bpy)(CN)_4]^-$

1.05.2013 - 15.12.2013

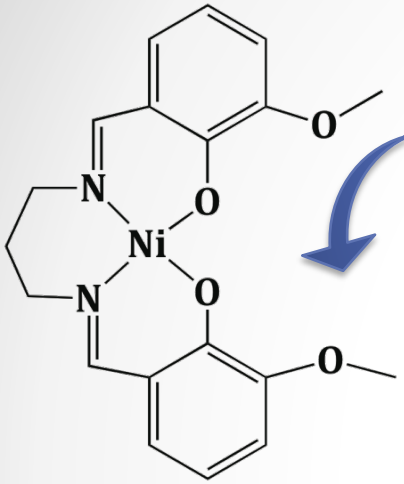
Heteroleptic metalloligands



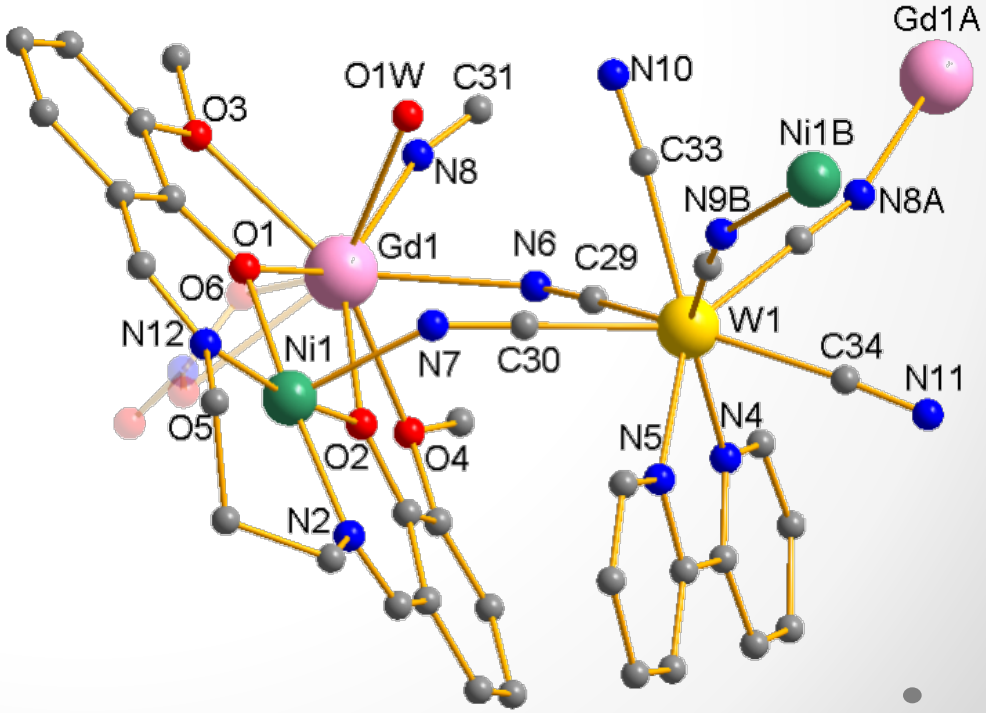
$[W(bpy)(CN)_6]^-$

- Synthesis and crystallo-genesis of coordination compounds based on $[W(bpy)(CN)_6]^-$ complex anion
- Spectral characterization and crystal structure
- Magnetic properties

$[W(bpy)(CN)_6]^- \longrightarrow$ 2-D {NiLnW} heterotrimetallic networks

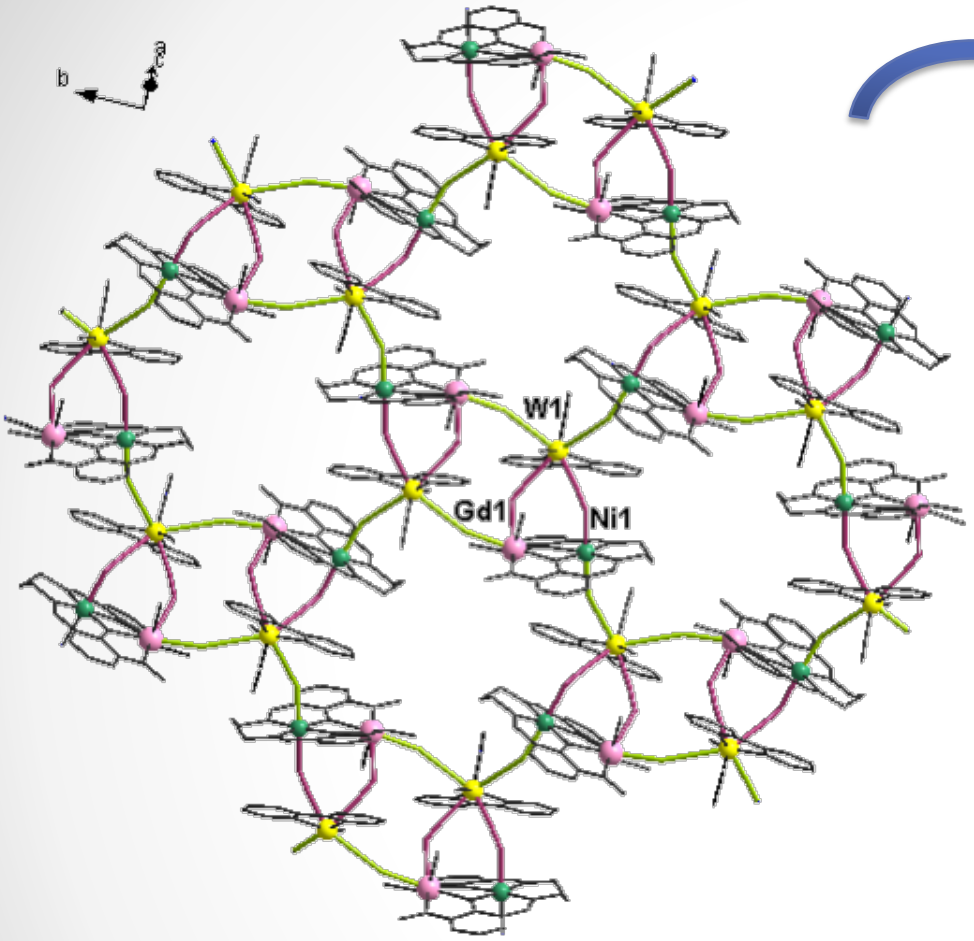


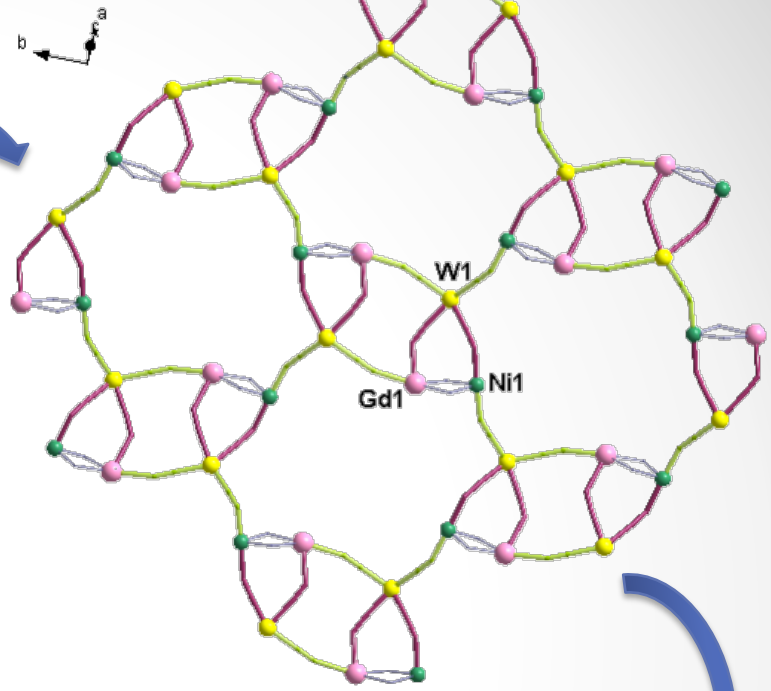
$Ln(NO_3)_3 + (Ph_4P)[W^V(bpy)(CN)_6]$

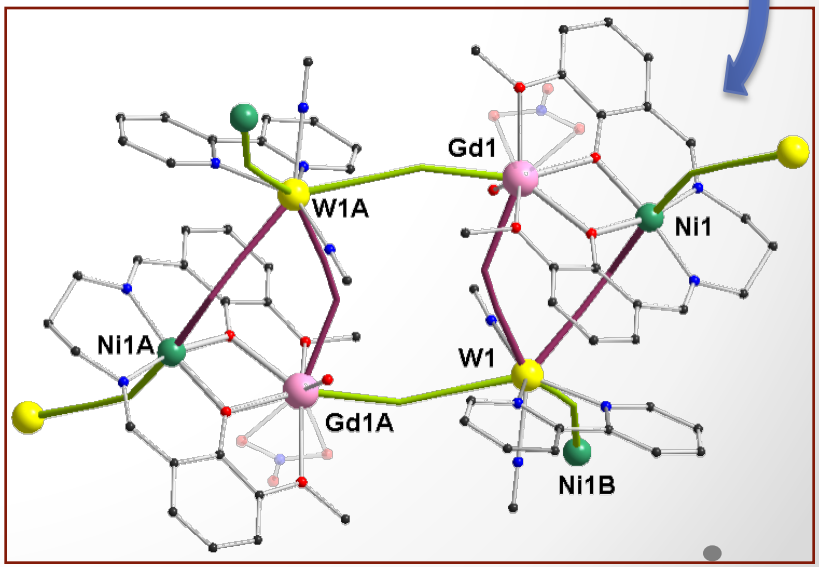


Ln(III) = Gd(**1**), Dy(**2**), Tb(**3**)

{NiLnW} – 2-D networks

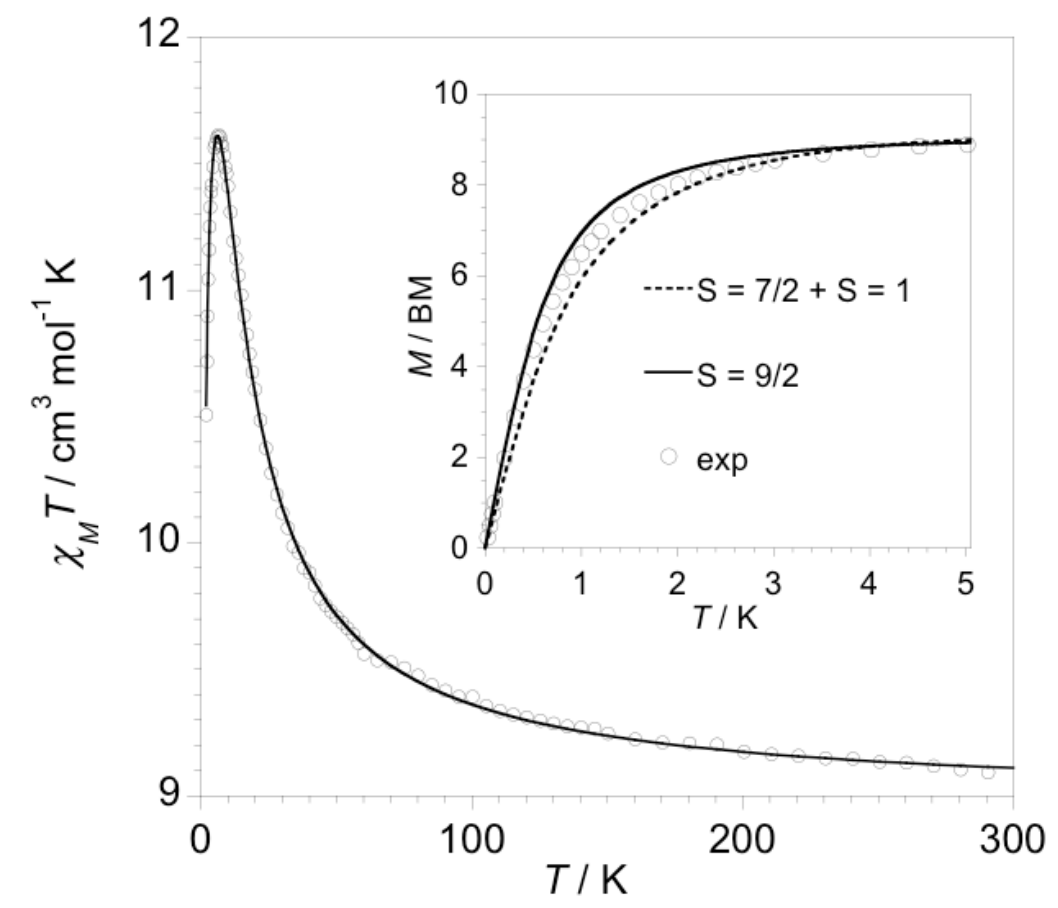






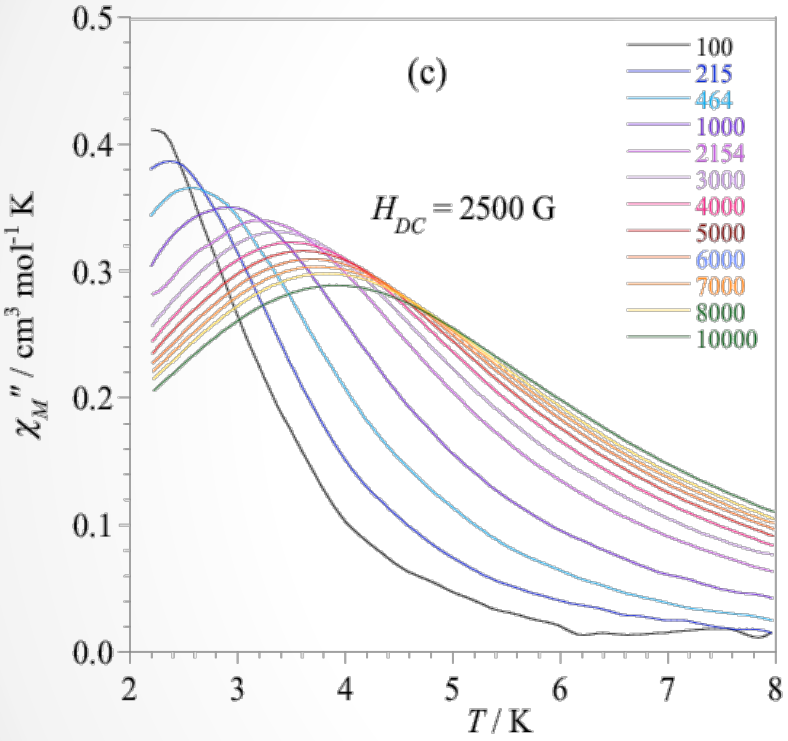
Structure of {**NiGdW**}. Left above: fragment of the structure showing the trinuclear units (plum), the hexanuclear fragments (plum/yellow). Left below: detail showing a hexanuclear unit.

Magnetic properties - dc measurements

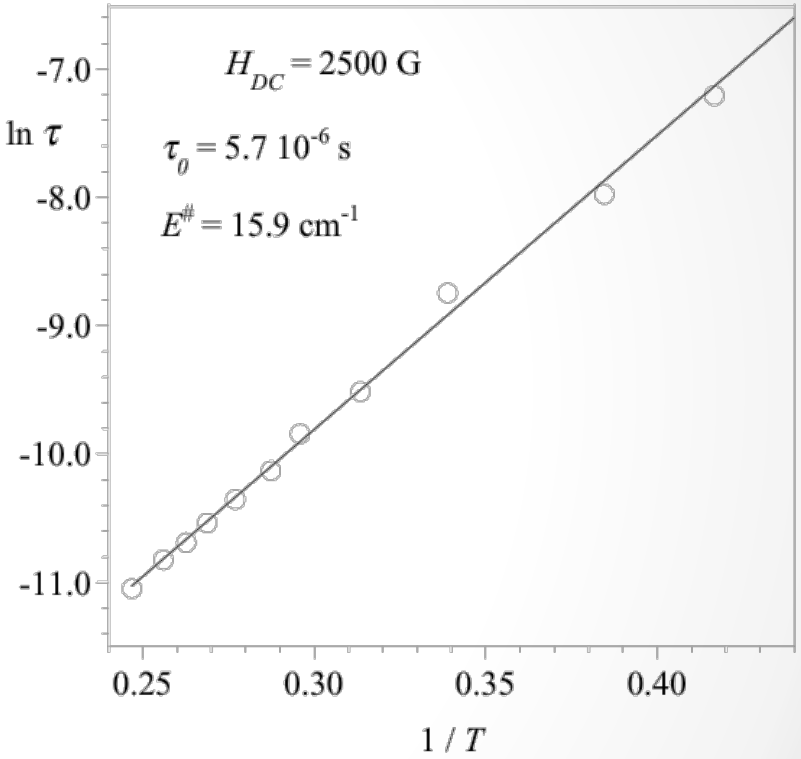


Thermal dependence of $\chi_M T$ for **1**: (o) experimental data, (–) best-fit curve. The inset shows the field dependence of the magnetization at 2.0 K: (o) experimental data; (--) theoretical curve for isolated Ni(II) and Gd(III) ions; (–) theoretical line for an $S = 9/2$ with $g = 2.0$)

ac measurements – showing the nanomagnet behavior of the Dy(III) derivative (2)



Frequency and temperature dependence of the out-of-phase magnetic susceptibility under external applied dc magnetic fields 2500 G for



Arrhenius plot as lnτ vs 1/T at 2500 G applied dc magnetic fields for **2**

Work in progress…

3*d* heteroleptic building-block → polynuclear networks

$(Ph_4P)[Fe^{III}(AA)(CN)_4]$ +

AA = phen, bpy

$Cu(valpn) + Ln(NO_3)_3$ → **$Fe^{III}_2(CuLn^{III})$**; Ln = Gd, Dy, Tb

- single crystals
- EDAX Fe:Cu:Ln = 2:1:1
- FTIR

$Ni(valpn) + Ln(NO_3)_3$ → **$FeNiLn^{III}$**; Ln = Gd, Dy, Tb

- single crystals
- EDAX (Fe:Ni:Ln = 1:1:1)
- FTIR

Results

All the activities scheduled for 2013 (8 months) were successfully fulfilled:

- The cyanido precursors were synthesized and were further employed in the crystallogenesis of the polynuclear complexes.
- The spectral characterization, as well as X-ray crystal diffraction analysis for the polynuclear coordination compounds were performed.
- The magnetic measurements in direct and alternating magnetic field showed an interesting case of a bidimensional heterotrimetallic network, $\{Ni^{II}Dy^{III}W^{IV}bpy\}$, exhibiting slow relaxation of the magnetization – a 2D framework of single-molecule magnets (SMM)

Dissemination

Papers

M.-G. Alexandru, D. Visinescu, S. Shova, F. Lloret, M. Julve, M. Andruh, *Two-Dimensional Coordination Polymers Constructed by $[Ni^{II}Ln^{III}]$ Nodes and $[W^{IV}(bpy)(CN)_6]^{2-}$ Spacers: A Network of $[Ni^{II}Dy^{III}]$ SMMs*, Inorg. Chem. **2013**, *52*, 11627- 11637. (FI = 4.6)

Conferences

D. Visinescu, **M.-G. Alexandru**, A. Madalan, M. Andruh, *Towards Heterotrimetallic Nanomagnets*, RICCCE 18, Sinaia, 4-7 septembrie 2013.

D. Visinescu, **M.-G. Alexandru**, A. Madalan, B. Jurca, M. Andruh, J. P. Sutter, R. Clérac, *New molecular-based magnetic materials. Towards heterotrimetallic nanomagnets*, RomPhysChem 15, Bucuresti, 11-13 september 2013.

M.-G. Alexandru, D. Visinescu, S. Shova, F. Lloret, M. Julve, M. Andruh, *Two-Dimensional Coordination Polymers Constructed by $[Ni^{II}Ln^{III}]$ Nodes and $[W^{IV}(bpy)(CN)_6]^{2-}$ Spacers,* RomPhysChem 15, Bucuresti, 11-13 september 2013.

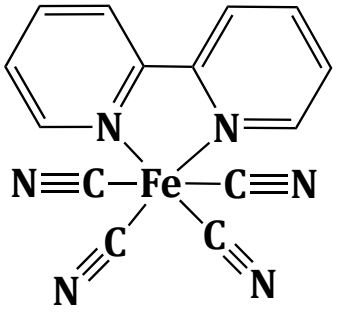
Stages abroad

- ✓ I participated in *The Zürich School of Crystallography,* which took place at the Institute of Organic Chemistry, University of Zurich, June, 9-22. I attended theoretical and practical classes due to which I have learned and gained new skills regarding X-ray diffraction on single crystals.

- ✓ Between 22rd June - 4th August, I had the opportunity to carry out a research stage at the University of Valencia. During this stage magnetic measurements were performed and the magnetic data analyzed.

1.05.2013 - 15.12.2013

Heteroleptic 3d metalloligands



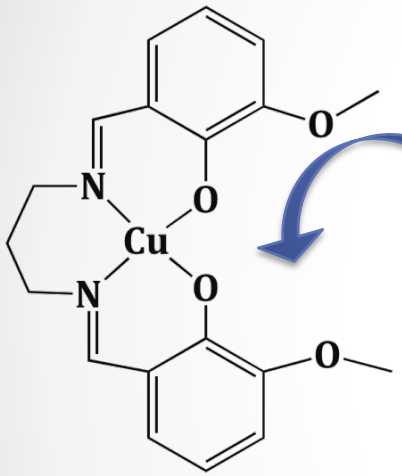
$Fe(bpy)(CN)_4]^-$

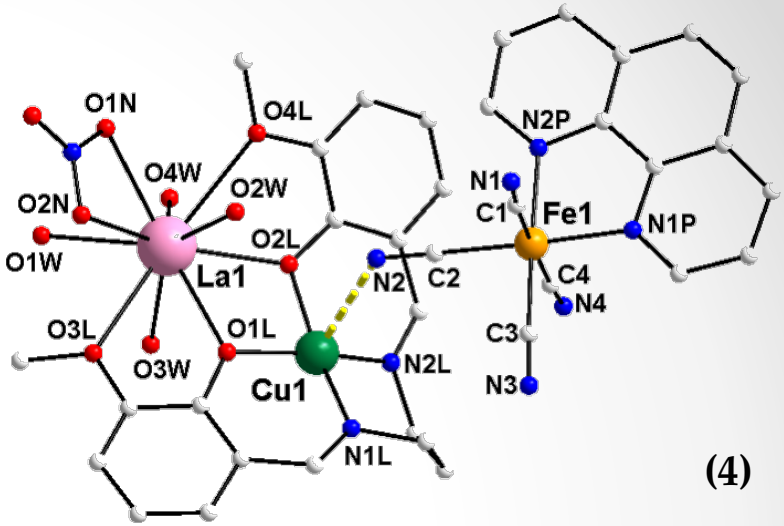
and

$Fe(phen)(CN)_4]^-$

- Synthesis and crystallo-genesis of coordination compounds based on $[Fe(bpy)(CN)_4]^-$ and $[Fe(phen)(CN)_4]^-$ complex anions
- Spectral characterization and crystal structure
- Magnetic properties

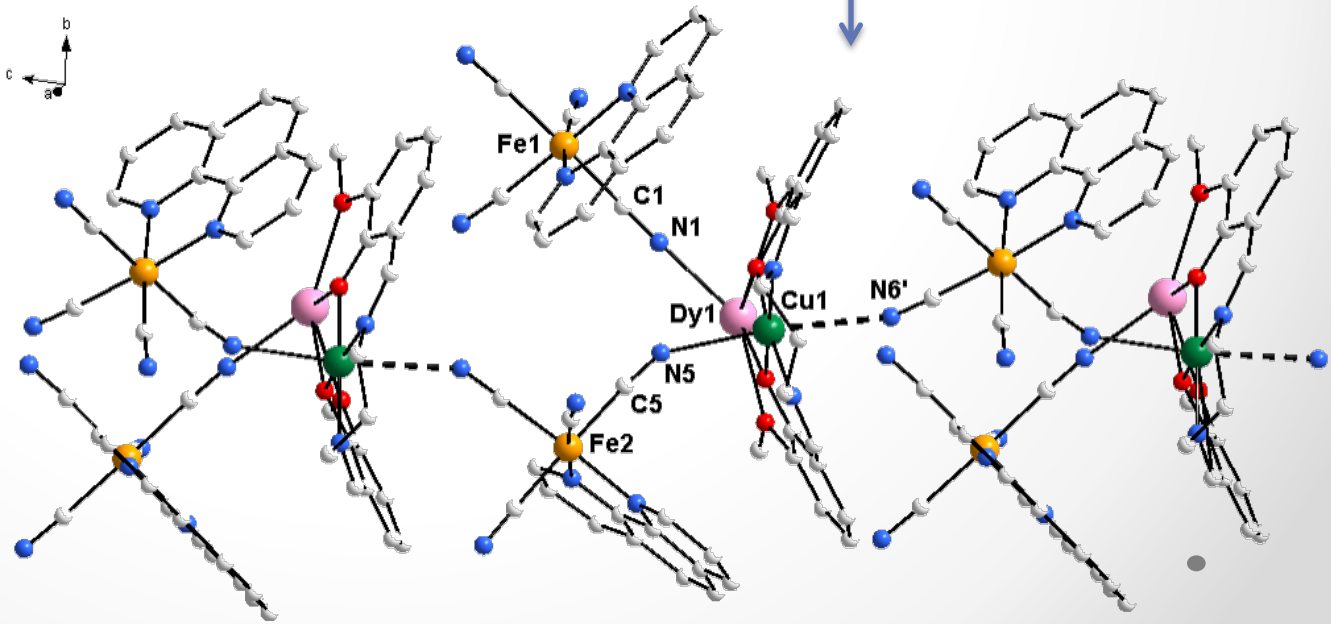
$[Fe(phen)(CN)_4]^-$ → 2-D {CuLnFe} heterotrimetallic coordination polymers





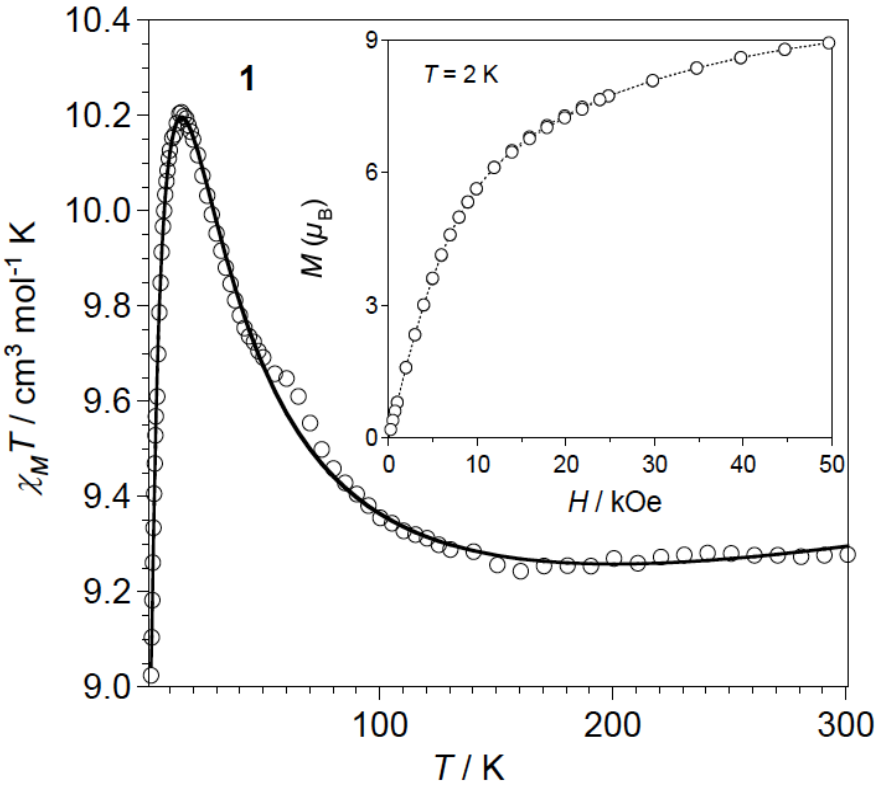
(4)

$Ln(NO_3)_3 + (Ph_4P)[Fe^{III}(phen)(CN)_4]$



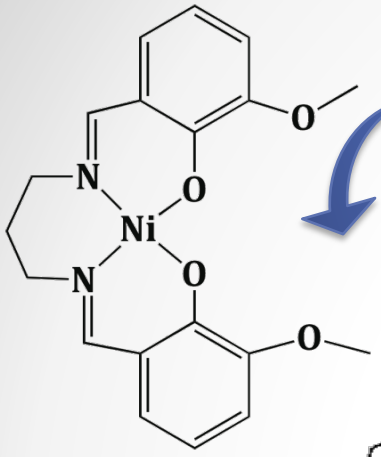
Ln = Gd (1), Tb (2), Dy (3)

Magnetic properties - dc measurements for the Gd(III) derivative

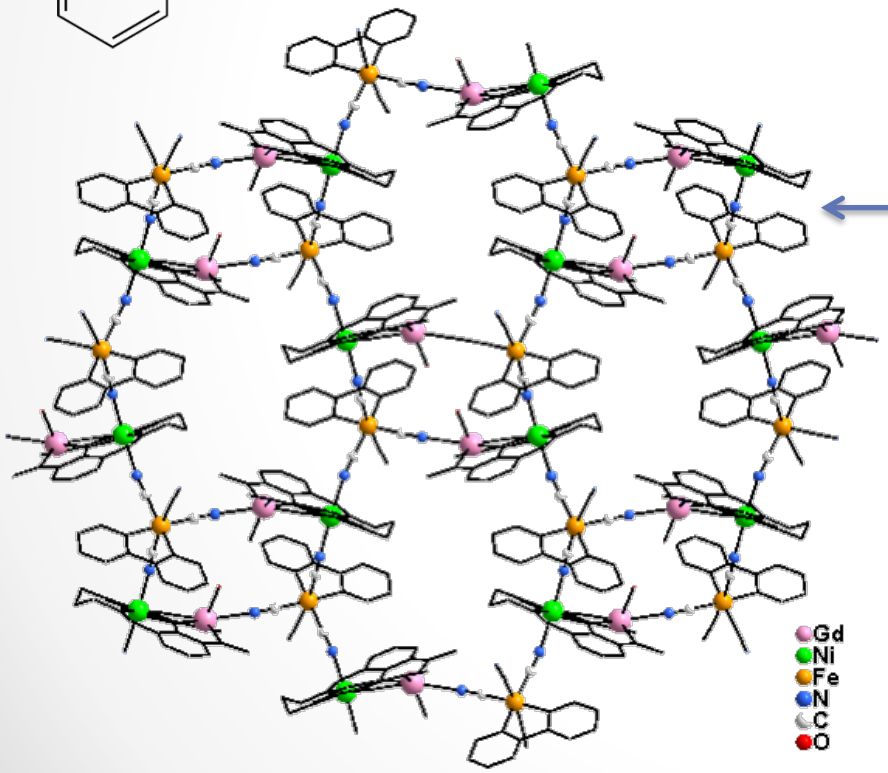


$\chi_M T$ *vs* T plot for **1**: (o) experimental; (—) best-fit curve. The inset shows the magnetization against H plot for **1** at 2.0 K (the dotted line is an eye-guide).

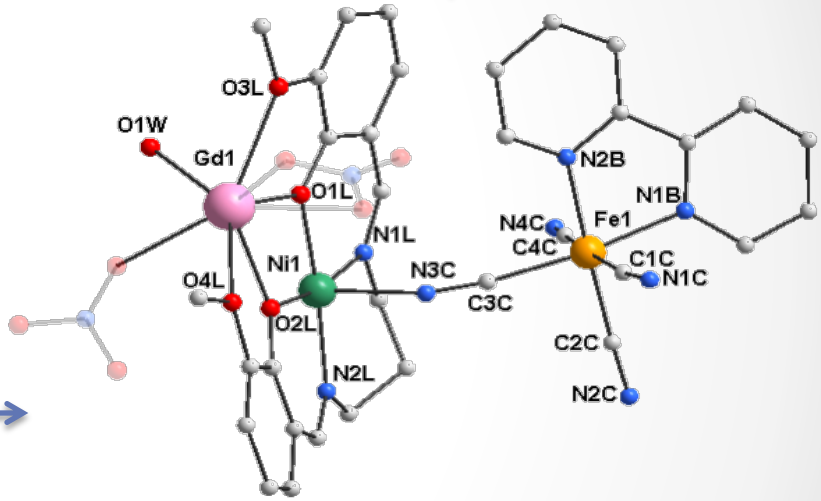
$[Fe(bipy)(CN)_4]^-$ ⟶ 2-D {NiLnFe} heterotrimetallic 2-D coordination polymers



$Ln(NO_3)_3 + (Ph_4P)[Fe^{III}(bpy)(CN)_4]$



View along the crystallographic *c* axis of a fragment of the 2D structure of **5**

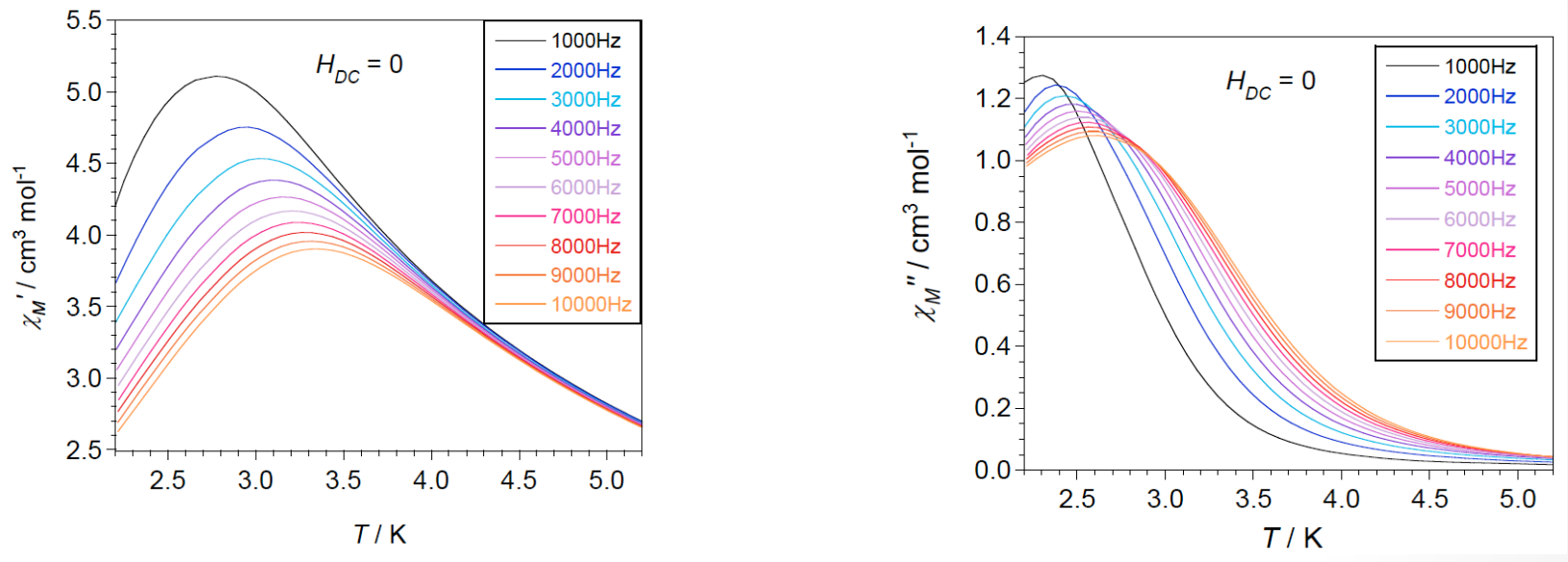


Asymmetric unit of **5**

Ln = Gd (5), Tb (6), Dy (7)

ac measurements – showing the nanomagnet behavior of the Tb(III) derivative, 6

2-D network of Single Chain Magnets



Temperature dependence of the in phase and out-of-phase (right) ac susceptibilities for **6** under a zero applied static field with a ±3.95 G oscillating field at frequencies in the range 1000-10000 Hz

Dissemination

Conferences

D. Visinescu, **M.-G. Alexandru**, M. Andruh, N. Marino, J. Vallejo, F. Lloret, M. Julve, *Two-dimensional {Ni(II)Ln(III)Fe(III)} heterotrimetallic coordination polymers*, ICMM, *Sankt Petersburg*, Rusia, 4-11 iulie 2014.

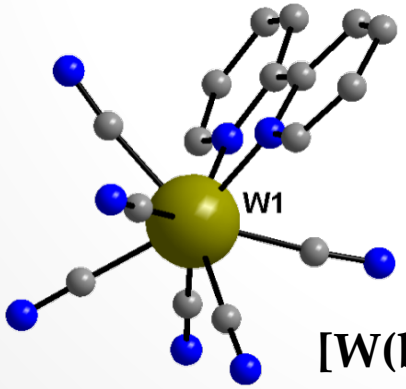
M.-G. Alexandru, D. Visinescu, M. Andruh, D. Armentano, J. Vallejo, F. Lloret, M. Julve, *{CuIILnIIIFeIII} heterotrimetallic coordination polymers,* 8ème Colloque Franco-Roumain de Chimie Appliquée (COFrRoCA), *Montpellier,* Franta, 14 – 19 septembrie 2014.

15.12.2014 - 31.10.2015

The aim is to obtain complexes which exhibit:

- photoinduced and thermally induced electron transfer process
- spin crossover phenomenon.

The heteroleptic cyanido complex, $\{W^{IV,V}(bpy)(CN)_6\}$, is being used as metalloligand to construct heterometallic coordination compounds.

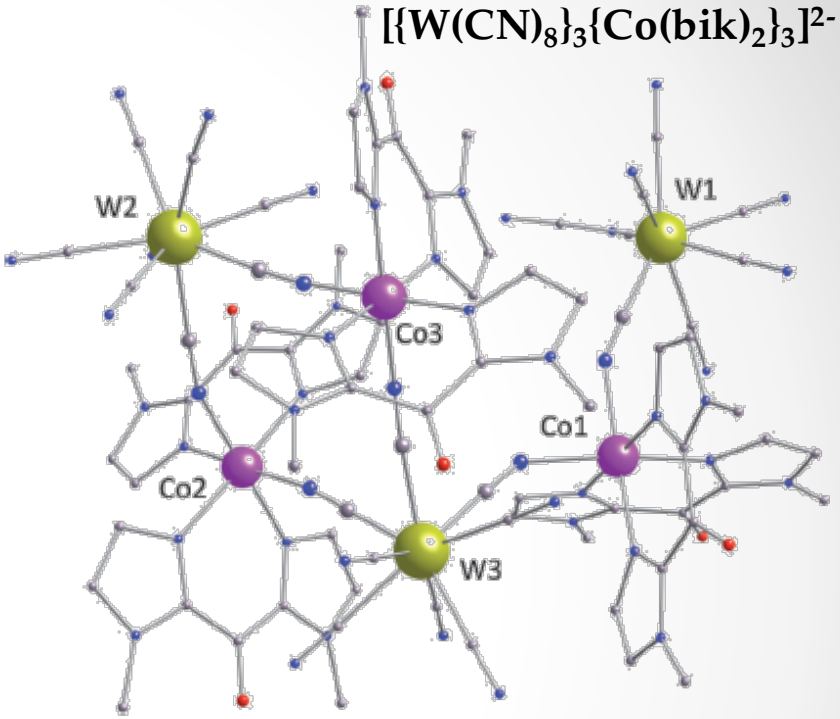


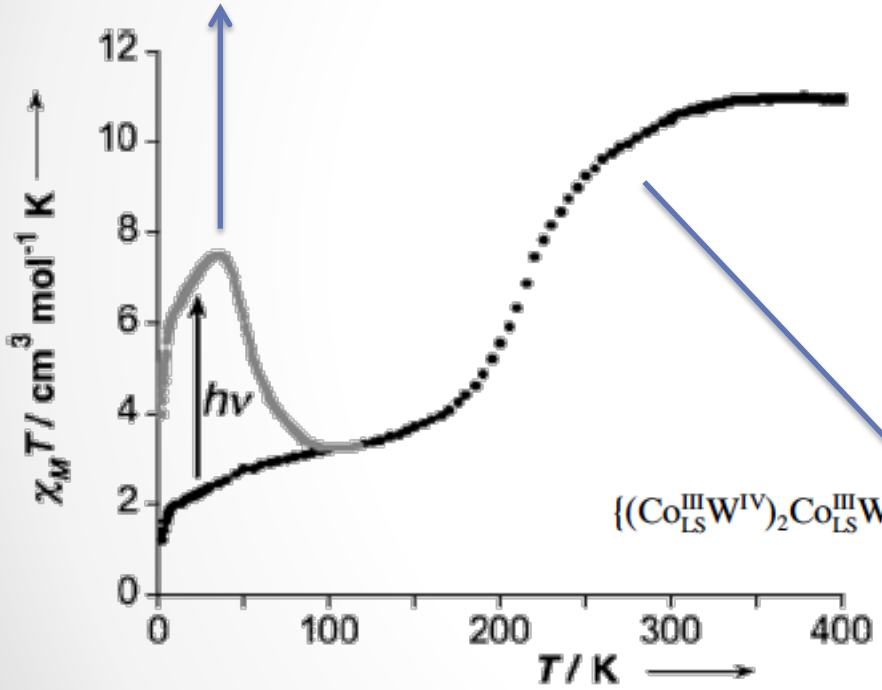
$[W(bpy)(CN)_6]^-$

Photomagnetism – light induced magnetization. Mechanism.

Photo-induced Electron Transfer Coupled Spin Transition
W^{IV}-CN-Co^{III}_{LS} to W^{V}-CN-Co^{II}_{HS}

$[\{W(CN)_8\}_3\{Co(bik)_2\}_3]^{2-}$





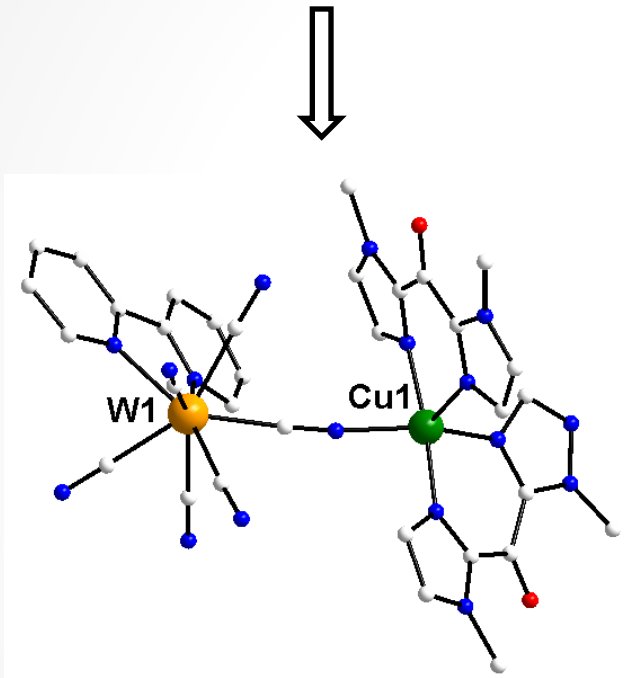
$\{(Co^{III}_{LS}W^{IV})_2Co^{III}_{LS}W^{V}\} \leftrightarrow \{(Co^{II}_{HS}W^{V})_2Co^{III}_{LS}W^{V}\}$

Thermally-induced electron transfer

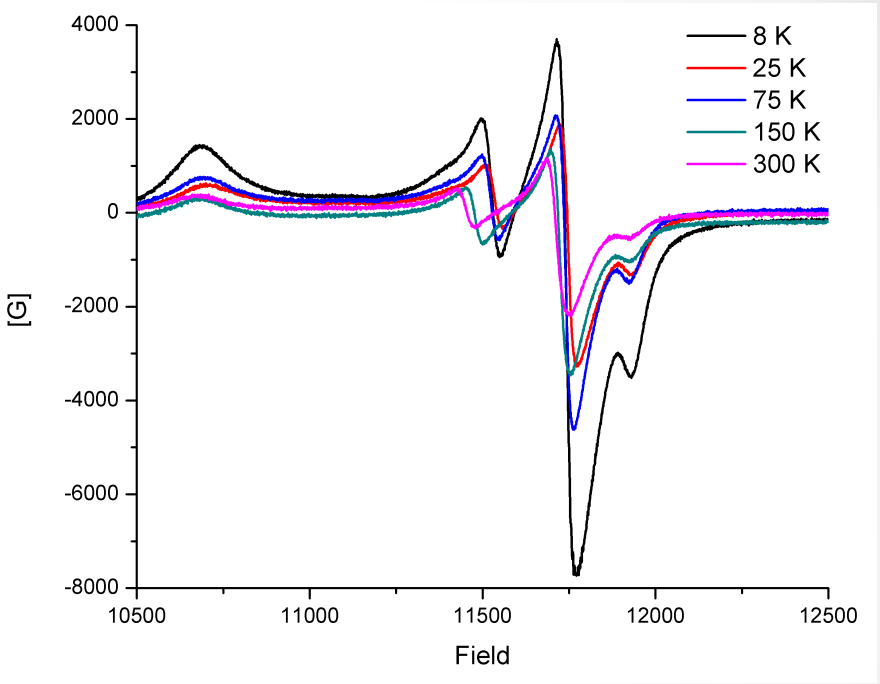
A. Mondal, L.-M. Chamoreau, Y. Li, Y. Journaux, M. Seuleiman, R. Lescouëzec, *Chem. Eur. J.* **2013**, *19*, 7682

W(IV)-M(II,III) structures

$Ph_4As[W(bpy)(CN)_6] + M(BF_4)_2 + 2bik$



$Cu^{II}(bik)_2(\mu\text{-}NC)W^{IV}(bpy)(CN)_5$



EPR spectrum

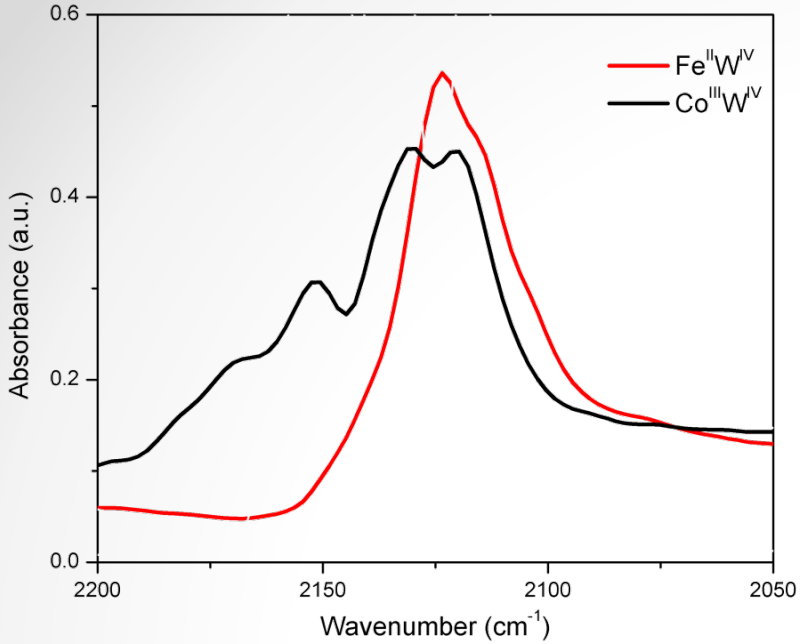
Cu(II) – distorted coordination geometry between square pyramidal and trigonal bipyramidal

M(II) = Cu, Co, Fe, Mn

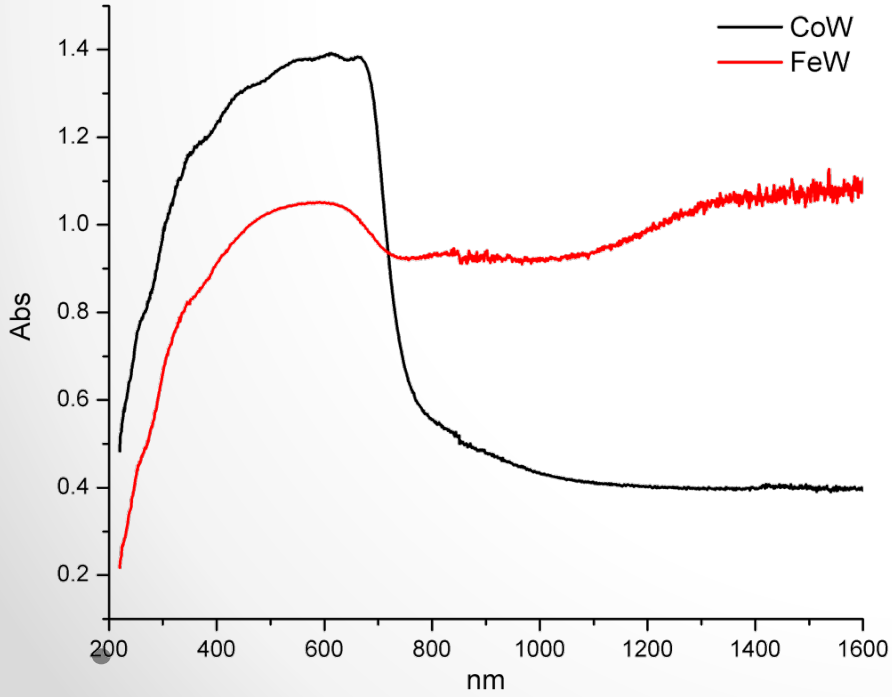
Magnetic measurements are in progress

W(IV)-M(II,III) structures

Spectral characterization

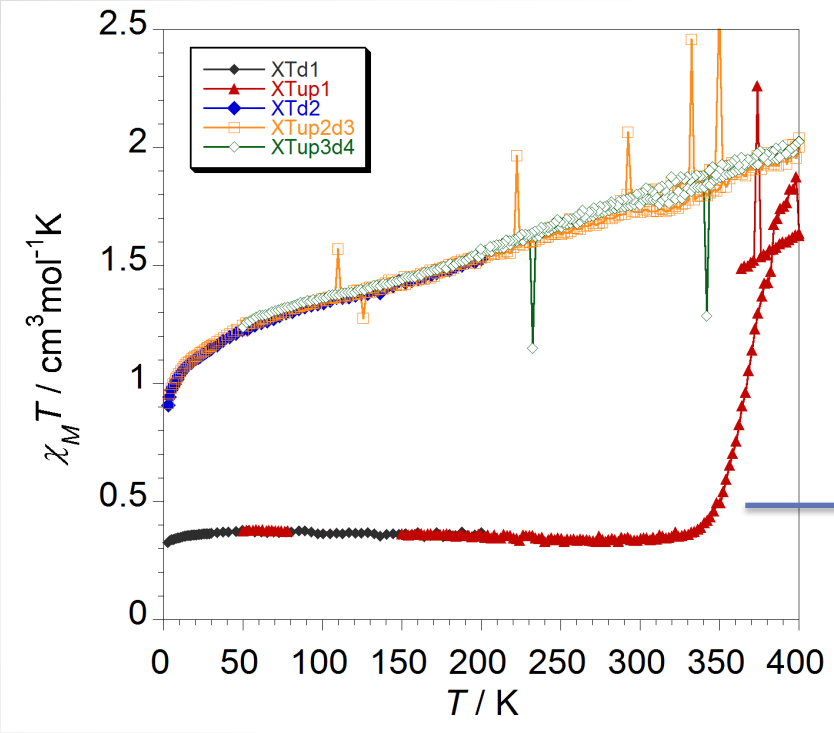


FTIR spectra of the Fe(II) and Co(III) derivatives showing the stretching vibrations of the cyanide group



UV-Vis spectra for the Fe(II) and Co(III) derivatives showing the Metal to Metal Charge Transfer at ca. 550 nm

Magnetic properties. Thermally-induced magnetization



Magnetic measurements under light irradiation and heating were performed for the $\{Co^{III}W^{IV}\}$ complex.

Thermally-induced electron transfer

$[W^{V}(bpy)(CN)_4]_2[Co^{III}(bik)_2]_2[(\mu\text{-}NC)_2W^{IV}(bpy)(CN)_4]_2$

$[W^{V}(bpy)(CN)_4]_2[Co^{II}_{HS}(bik)_2]_2[(\mu\text{-}NC)_2W^{V}(bpy)(CN)_4]_2$

Between 18rd June - 8th August, I had the opportunity to carry out a research stage at the University of Valencia. During this stage magnetic measurements were performed and the magnetic data analyzed.

Dissemination

Articles

M.-G. Alexandru, D. Visinescu, S. Shova, F. Lloret, M. Julve, M. Andruh, *Heterotrimetallic coordination polymers: {$Cu^{II}Ln^{III}Fe^{III}$} chains and {$Ni^{II}Ln^{III}Fe^{III}$} layers. Synthesis, crystal structures and magnetic properties*, Chemistry-A European Journal, **2015** *21*, 5429; FI = 5.69

Conferences

M.-G. Alexandru, M. Andruh, *Heteroleptic Cyanido Metalloligands – toward New Magnetic Molecular Materials*, RICCCE, 2-5 septembrie 2015, Sibiu – keynote lecture