
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 heterotrtrimetallic 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.
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 ($\chi'$) and out-of-phase ($\chi''$) 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

Node and spacer approach → heterometallic complexes

M1 = 3d metal ion
M2 = 3d or 4f metal ion

Homoleptic

M(V) = Mo, W

Heteroleptic

[Fe(bpy)(CN)_4]^-
1.05.2013 - 15.12.2013

Heteroleptic metalloligands

- Synthesis and crystallo-genesis of coordination compounds based on \([W(bpy)(CN)_6]^-\) complex anion
- Spectral characterization and crystal structure
- Magnetic properties
$[\text{W(bpy)(CN)}_6]^{-} \rightarrow 2$-D $\{\text{NiLnW}\}$ heterotrimetallic networks

$\text{Ln(NO}_3)_3 + (\text{Ph}_4\text{P})[\text{W}^v(\text{bpy})(\text{CN})_6]$}

$\text{Ln(III)} = \text{Gd(1)}, \text{Dy(2)}, \text{Tb(3)}$
Structure of \{\text{NiGdW}\}. Left above: fragment of the structure showing the trinuclear units (plum), the hexanuclear fragments (plum/yellow). Left below: detail showing a hexanuclear unit.
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 $g = 2.0$.
Frequency and temperature dependence of the out-of-phase magnetic susceptibility under external applied dc magnetic fields 2500 G for ac measurements – showing the nanomagnet behavior of the Dy(III) derivative (2)

Arrhenius plot as \( \ln \tau \) vs \( 1/T \) at 2500 G applied dc magnetic fields for 2
Work in progress...

3d heteroleptic building-block → polynuclear networks

(Ph₄P)[Fe³⁺(AA)(CN)₄] + AA = phen, bpy

Cu(valpn) + Ln(NO₃)₃ → Fe³⁺₂(CuLn³⁺); Ln = Gd, Dy, Tb
- single crystals
- EDAX Fe:Cu:Ln = 2:1:1
- FTIR

Ni(valpn) + Ln(NO₃)₃ → FeNiLn³⁺; 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, \(\{\text{Ni}^{II}\text{Dy}^{III}\text{W}^{IV}\text{bpy}\}\), 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 \([\text{Ni}^{II}\text{Ln}^{III}]\) Nodes and \([\text{W}^{IV}(\text{bpy})(\text{CN})_6]^2\) Spacers: A Network of \([\text{Ni}^{II}\text{Dy}^{III}]\) 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.


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 22\textsuperscript{rd} June - 4\textsuperscript{th} 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.
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)$_4$]$^-$ $\rightarrow$ 2-D \{CuLnFe\} heterotrismetallic coordination polymers

Ln(NO$_3$)$_3$ + (Ph$_4$P)[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]^− \rightarrow 2-D \{\text{NiLnFe}\} \text{ heterotrimetallic 2-D coordination polymers}

\text{Ln(NO}_3\text{)}_3 + (\text{Ph}_4\text{P})[\text{Fe}^{\text{III}}(\text{bpy})(\text{CN})_4] \rightarrow \text{Asymmetric unit of 5}

\text{Ln} = \text{Gd} (5), \text{Tb} (6), \text{Dy} (7)

View along the crystallographic c axis of a fragment of the 2D structure of 5
Temperature dependence of the in phase and out-of-phase (right) ac susceptibilities for 6 under a zero applied static field with a $\pm 3.95$ G oscillating field at frequencies in the range 1000-10000 Hz
Dissemination

Conferences


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.
Photomagnetism – light induced magnetization. Mechanism.

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

$\chi_M T / \text{cm}^3 \text{mol}^{-1} \text{K}$

$\{(\text{Co}^{III}_{LS}W^{IV})_2\text{Co}^{III}_{LS}W^{V}\} \leftrightarrow \{(\text{Co}^{II}_{HS}W^{V})_2\text{Co}^{III}_{LS}W^{V}\}$

Thermally-induced electron transfer

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

$\text{Ph}_4\text{As}[\text{W(bpy)(CN)}_6] + \text{M(BF}_4)_2 + 2\text{bik}$

$\text{Cu}^{II} - \text{distorted coordination geometry between square pyramidal and trigonal bipyramidal}$

EPR spectrum

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

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

W(IV)-M(II,III) structures
Spectral characterization
Magnetic properties. Thermally-induced magnetization

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

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

\[
\text{[W}^{\text{V}}\text{(bpy)(CN)}_4]\text{[Co}^{\text{II}}\text{HS(bik)}_2\text{][(µ-NC)}_2\text{W}^{\text{V}}\text{(bpy)(CN)}_4]\text{]_2}
\]
Between 18th 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