UNIVERSITATEA DIN BUCUREȘTI

VIRTUTE ET SAPIENTIA

A NEW GENERATION OF MOLECULAR MAGNETIC MATERIALS CONSTRUCTED FROM 2p SPIN CARRIERS AND METAL IONS

Financial support: UEFISCDI

UEFISCDI
INOVARE SI CREATIVITATE
UNITATEA EXECUTIVA PENTRU FINANTAREA INVATAMANTULUI SUPERIOR, A CERCETARII DEZVOLTARII SI INOVARII

Project Code: PN-III-P4-ID-PCE-2016-0308 (92/2017)

Project timespan: 2017 – 2019

Project Team

Project leader: Acad. Marius Andruh

Members:

- **CS III Catalin Maxim**
- **CS III Delia-Laura Popescu**
- **CS III Ruxandra Gheorghe**
- **Drd. Andrei Alunel Patrascu**
- **Drd. Mihaela Mocanu**
- **MSc student Adela Spinciu**
- **MSc student Diana Eftemie**

Project Budget

No.	BUDGET CHAPTER (EXPENSES)	2017 (lei)	2018 (lei)	2019 (lei)	TOTAL (lei)
1	SALARIES	89.002,00	150.000,00	110.998,00	350.000,00
2	INVENTORY	129.278,00	100.000,00	25.722,00	255.000,00
3	MOBILITY	15.000,00	30.000,00	30.000,00	75.000,00
4	OVERHEAD	58.320,00	70.000,00	41.680,00	170.000,00
	TOTAL BUDGET	**291.600,00**	**350.000,00**	**208.400,00**	**850.000,00**

Abstract

Most of the heterospin complexes with nitronyl-nitroxide ligands are assembled using 3d and 4f metals. Heterotrispin systems constructed from one radical (nitronyl-nitroxides, tempo derivatives) and two different paramagnetic metal ions are very scarce. The interest in such compounds arises from their magnetic properties and, ultimately, when acting as nanomagnets, from their potential ability to store and process information at molecular level. We intend to develop synthetic strategy to generate heterospin 2p-3d-4f complexes with a pre-established number of spin carriers. By choosing the appropriate metals we can a priori modulate the magnetic properties. Such discrete species are excellent candidates for magneto-structural correlations. The number of known 2p-3d-4f complexes is very low, and new examples are needed to get more insight into their magnetic behavior. Two main directions towards heterospin 2p-4f, 2p-3d, and especially, 2p-3d-4f complexes will be pursued from the following families of precursors: (1) heterobinuclear 3d-4f complexes containing the {LnIII(hfac)2(CH3COO)} moiety. The synthetic approach relies on selective substitution of one anionic ligand (acetato) from the coordination sphere of the lanthanide ion by an anionic radical; (2) an original family of heterotopic end-off compartmental ligands which can selectively interact with 3d and 4f ions, leading to predictable heterospin complexes. One compartment is made by a Mannich-base moiety, while the other is generated by nitronyl-nitroxide pendant arm. The leading idea of the project is to develop a synthetic strategy for 2p-3d-4f complexes that can open new perspectives in molecular magnetism as well as in the chemistry of multifunctional molecular materials. From the synthetic point of view, the project is expected to have a strong impact, since we propose an original strategy for obtaining 2p-3d-4f heterospin complexes, based on unprecedented ligands.

Objectives

The present project aims to synthesize novel 2p-3d-4f heterotrispin complexes, following two original strategies:

(1) self-assembly processes involving 3d-4f precursors and paramagnetic organic radicals;

(2) design of compartmental nitronyl-nitroxide ligands and their reactions with 3d and 4f metal ions.

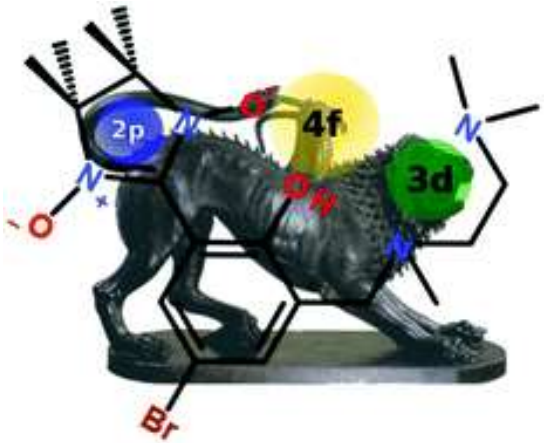
The ultimate objective of the project consists of synthesis and characterization of new molecular nano-magnets.

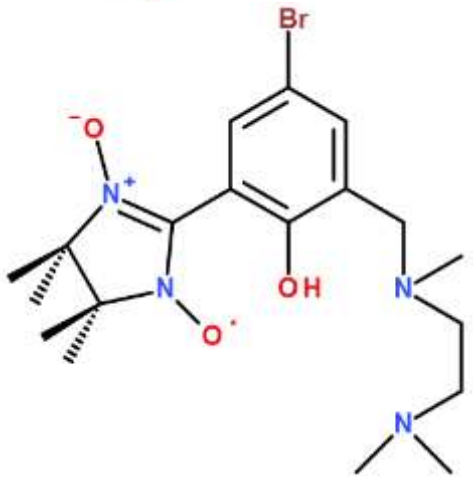
A special emphasis will be given to the oligonuclear species that can serve as models for magneto-structural correlations, particularly for systems which are not investigated so far (e. g. Mn(II)-Ln(III)).

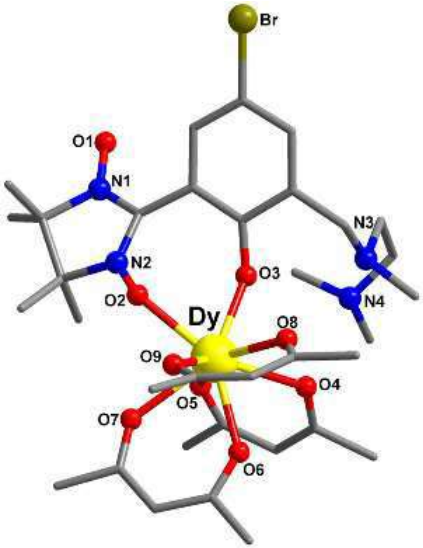
Chiral heterospin molecule-based magnets will be synthesized as well.

Major Scientific Results

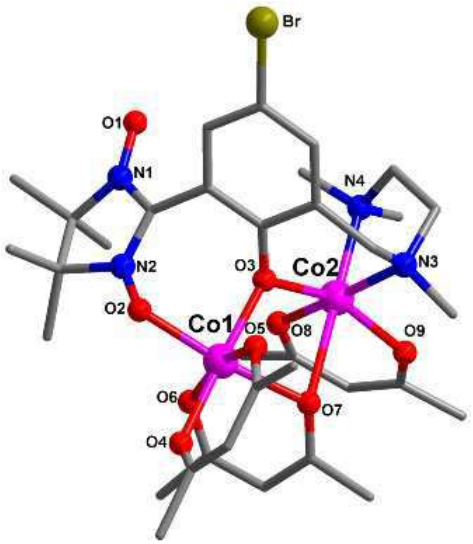
❑ **Design of heterospin 2p–3d, 2p–4f, and 2p–3d–4f complexes using a novel family of paramagnetic dissymmetric compartmental ligands**



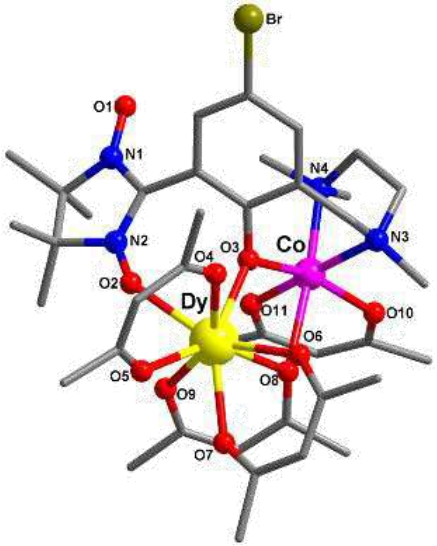




$[Dy(LH)(hfac)_3]$



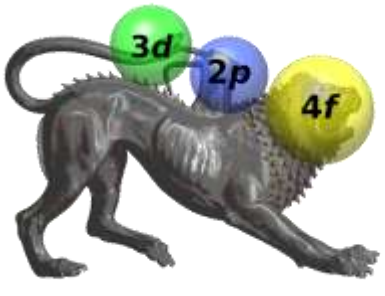
$[Co_2L(hfac)_3]$



$[CoDyL(hfac)_4]$

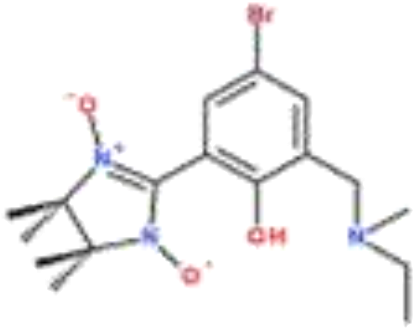
Major Scientific Results

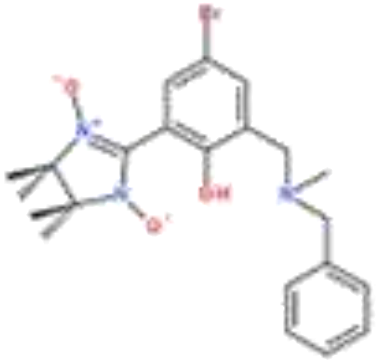
❑ **First 2p−3d−4f Heterotrispin Complexes with Different Metal Ions Bridged by One Aminoxyl Group**

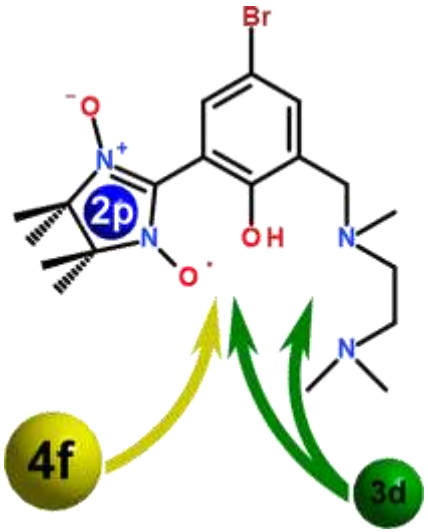


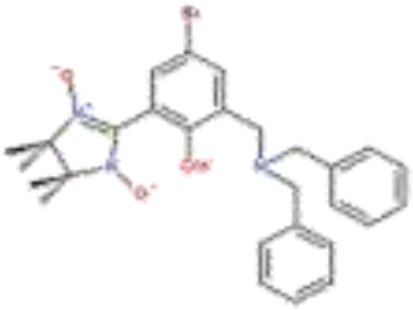
2017: J_{3d2p} ~ 0 cm^{-1}
~~SMM~~

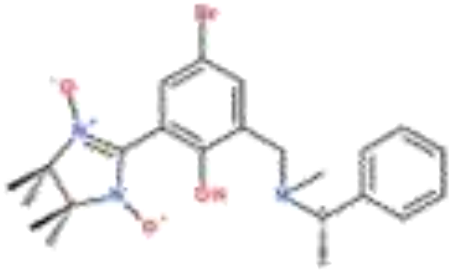
2019: J_{3d2p} ~ -20 cm^{-1}
SMM!







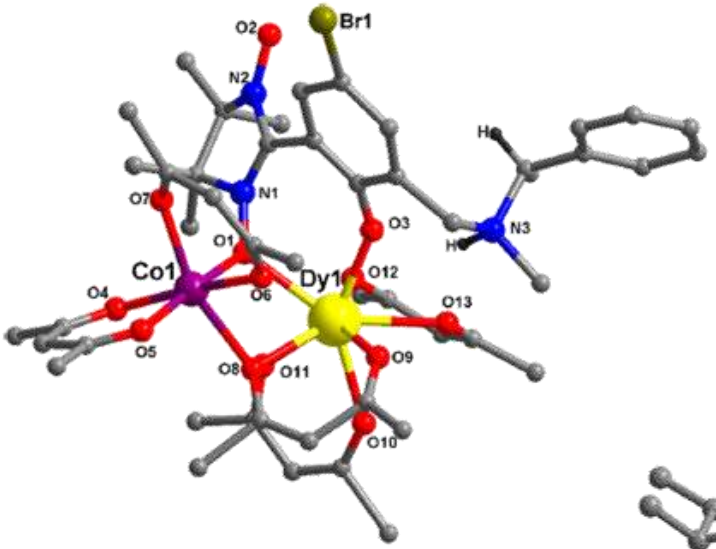




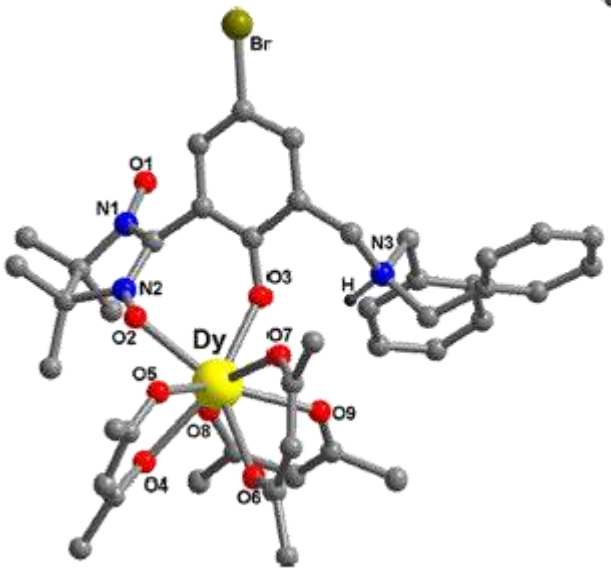
Nitronyl-Nitroxide-Mannich Base Proligands

Major Scientific Results

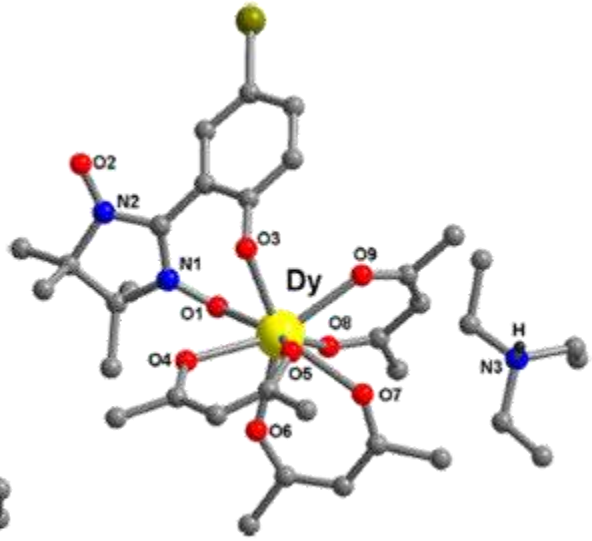
❑ **First 2p−3d−4f Heterotrispin Complexes with Different Metal Ions Bridged by One Aminoxyl Group**



$[Co^{II}Dy^{III}(R\text{-}L^{4}H)(hfac)_3]$



$[Dy(L^{3}H)(hfac)_3]$



$(HNEt_3)[DyL(hfac)_3]$

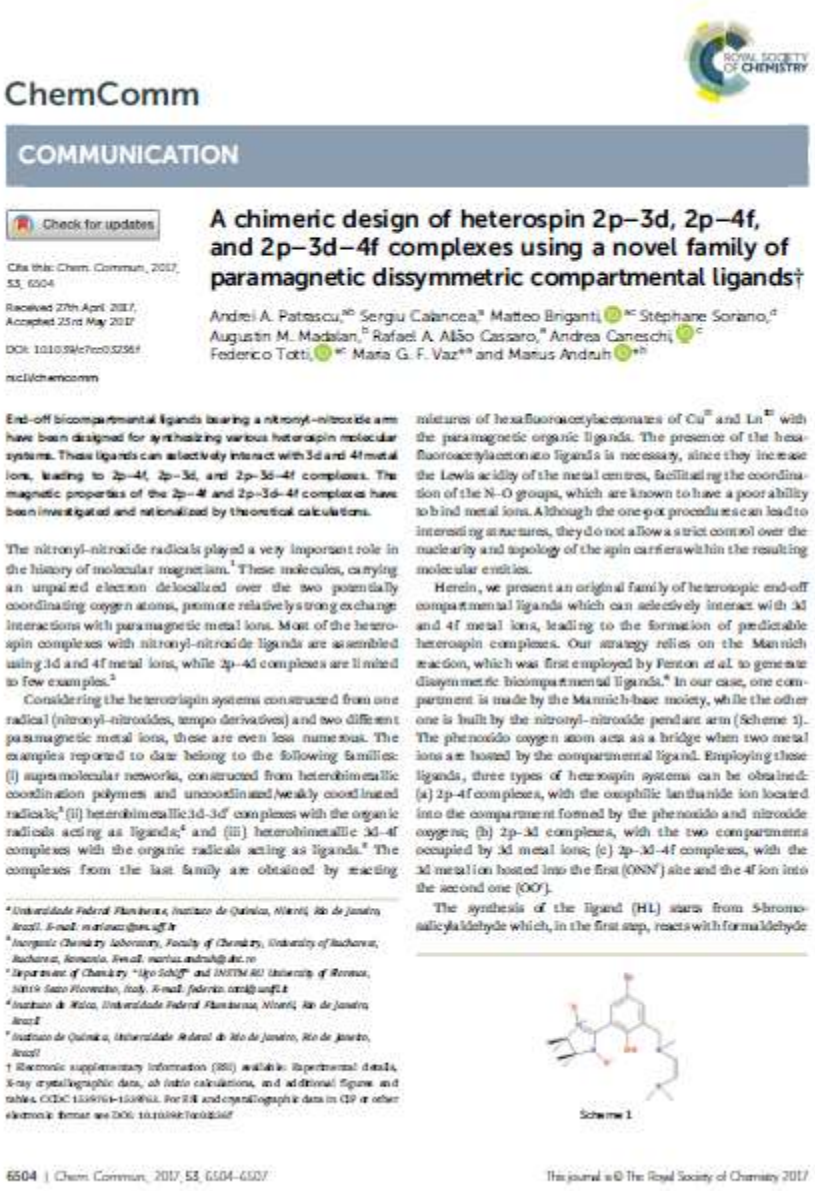
Dissemination of Results - 2017

Autori: Andrei A. Patrascu, Sergiu Calancea, Matteo Briganti, Stephane Soriano, Augustin M. Madalan, Rafael A. Allao-Cassaro, Andrea Caneschi, Federico Totti, Maria G.F. Vaz, Andruh Marius

Titlul articolului: *A chimeric design of heterospin 2p–3d, 2p–4f, and 2p–3d–4f complexes using a novel family of paramagnetic dissymmetric compartmental ligands*

Chem. Commun., 2017, 53, 6504- 6507

The authors acknowledge FAPERJ, CAPES, CNPq, and UEFISCDI for the financial support. A. Patrascu and M. Briganti acknowledge FAPERJ–Programa de doutorado Sanduiche Reverso (Project E-26/200.028/2015 and Project E-26/200.104/2016) for the fellowship. We are also grateful to LDRX-UFF and CENAPAD-SP (proj 627) for the use of their facilities. Dr F. Totti acknowledges the European Research Council Grant MolNanoMas (grant no. 267746), the internationalization program of University of Florence (IFUND2015 no. 399 and PIA2013-15) and S. Soriano thanks Conselho Nacional de Desenvolvimento Cientifico e Tecnológico (CNPq).



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rsc.li/chemcomm

A chimeric design of heterospin 2p–3d, 2p–4f, and 2p–3d–4f complexes using a novel family of paramagnetic dissymmetric compartmental ligands†

Andrei A. Patrascu,[ab] Sergiu Calancea,[a] Matteo Briganti,[bc] Stephane Soriano,[d] Augustin M. Madalan,[b] Rafael A. Allão Cassaro,[e] Andrea Caneschi,[c] Federico Totti,[bc] Maria G. F. Vaz*[e] and Marius Andruh*[b]

End-off bicompartmental ligands bearing a nitronyl–nitroxide arm have been designed for synthesizing various heterospin molecular systems. These ligands can selectively interact with 3d and 4f metal ions, leading to 2p–4f, 2p–3d, and 2p–3d–4f complexes. The magnetic properties of the 2p–4f and 2p–3d–4f complexes have been investigated and rationalized by theoretical calculations.

The nitronyl-nitroxide radicals played a very important role in the history of molecular magnetism.[1] These molecules, carrying an unpaired electron delocalized over the two potentially coordinating oxygen atoms, promote relatively strong exchange interactions with paramagnetic metal ions. Most of the heterospin complexes with nitronyl-nitroxide ligands are assembled using 3d and 4f metal ions, while 2p–4d complexes are limited to few examples.[2]

Considering the heterotrispin systems constructed from one radical (nitronyl-nitroxides, tempo derivatives) and two different paramagnetic metal ions, these are even less numerous. The examples reported to date belong to the following families: (i) supramolecular networks, constructed from heterobimetallic coordination polymers and uncoordinated/weakly coordinated radicals;[3] (ii) heterobimetallic 3d–3d′ complexes with the organic radicals acting as ligands;[4] and (iii) heterobimetallic 3d–4f complexes with the organic radicals acting as ligands.[5] The complexes from the last family are obtained by reacting mixtures of hexafluoroacetylacetonates of Cu^{II} and Ln^{III} with the paramagnetic organic ligands. The presence of the hexafluoroacetylacetonato ligands is necessary, since they increase the Lewis acidity of the metal centres, facilitating the coordination of the N–O groups, which are known to have a poor ability to bind metal ions. Although the one-pot procedure can lead to interesting structures, they do not allow a strict control over the nuclearity and topology of the spin carriers within the resulting molecular entities.

Herein, we present an original family of heterotopic end-off compartmental ligands which can selectively interact with 3d and 4f metal ions, leading to the formation of predictable heterospin complexes. Our strategy relies on the Mannich reaction, which was first employed by Fenton *et al.* to generate dissymmetric bicompartmental ligands.[6] In our case, one compartment is made by the Mannich-base moiety, while the other one is built by the nitronyl–nitroxide pendant arm (Scheme 1). The phenoxido oxygen atom acts as a bridge when two metal ions are hosted by the compartmental ligand. Employing these ligands, three types of heterospin systems can be obtained: (a) 2p–4f complexes, with the oxophilic lanthanide ion located into the compartment formed by the phenoxido and nitroxide oxygens; (b) 2p–3d complexes, with the two compartments occupied by 3d metal ions; (c) 2p–3d–4f complexes, with the 3d metal ion hosted into the first (ONN′) site and the 4f ion into the second one (OO′).

The synthesis of the ligand (HL) starts from 5-bromosalicylaldehyde which, in the first step, reacts with formaldehyde

Scheme 1

[a] Universidade Federal Fluminense, Instituto de Química, Niterói, Rio de Janeiro, Brazil. E-mail: marinas@vm.uff.br
[b] Inorganic Chemistry Laboratory, Faculty of Chemistry, University of Bucharest, Bucharest, Romania. E-mail: marius.andruh@dnt.ro
[c] Department of Chemistry "Ugo Schiff" and INSTM RU University of Florence, 50019 Sesto Fiorentino, Italy. E-mail: federico.totti@unifi.it
[d] Institute de Física, Universidade Federal Fluminense, Niterói, Rio de Janeiro, Brazil
[e] Instituto de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil

† Electronic supplementary information (ESI) available: Experimental details, X-ray crystallographic data, *ab initio* calculations, and additional figures and tables. CCDC 1558761–1558763. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7cc03256f

Dissemination of Results - 2017

Conferences

1. Marius Andruh, **Lanthanide-based homo- and heterometallic clusters**, 3rd International Conference on Functional Molecular Materials, Krakow, 8-10 November 2017 (*invited lecture*)

2. Andrei A. Patrascu, S. Calancea, M. Briganti, S. Soriano, A. M. Madalan, R. A. Allão Cassaro, A. Caneschi, F. Totti, M. G. F. Vaz, Marius Andruh, **Rational design of heterospin 2p-3d, 2p-4f, and 2p-3d-4f complexes using a novel family of paramagnetic dissymmetric compartmental ligands,** 6th Europen Conference on Molecular Magnetism (ECMM 2017), 27-31 August 2017, Bucharest, Romania (oral presentation).

3. Mihaela Mocanu, Andrei A. Patrascu, F. Llorent, M. Julve, Marius Andruh, **A new synthetic approach towards polynuclear complexes using mixed Schiff and Mannich base ligands,** 6th Europen Conference on Molecular Magnetism (ECMM 2017), 27-31 August 2017, Bucharest, Romania (poster).

Dissemination of Results - 2018

Conferences

1. Heterotrispin complexes. Looking for synergistic effects within 2p-3d-4f complexes, Marius Andruh - *Keynote lecture,* 16th International Conference on Molecule-based Magnets, Rio de Janeiro, Brazil, 1-5 September, 2018.

2. Heterostrispin 2p-3d-4f Complexes, Marius Andruh - *Invited lecture,* 8th International Conference High Spin Molecules and Molecular Magnets, Astrakhan, Russia, 17-21 September 2018.

3. Heterotrispin complexes. Looking for synergistic effects within 2p-3d-4f complexes, Marius Andruh - conferinta la Institutul de Chimie Chisinau, 12 octombrie 2018.

4. Looking for synergistic effects within 2p-3d-4f complexes, Marius Andruh - Universitatea Taras Sevcenco, Kiev, decembrie 2018.

Dissemination of Results - 2018

Conferences

5. Efecte sinergetice in complecsi heterotrispin 2p-3d-4f, Marius Andruh - Conferința Zilele Academice Clujene, 18-19 octombrie 2018.

6. Complecși Homo- și Heterometalici Construiți Utilizând Derivați Hexafluoroacetilacetonați și Complecși de Tip Bază Schiff ca unități de construcție, Mihaela Mocanu, Sergiu Shova, Francesc Lloret, Miguel Julve, Marius Andruh, Conferința Națională a Şcolilor Doctorale din Consorțiul Universitaria, 31 Octombrie-3 Noiembrie 2018, Iași, prezentare orală.

7. Homo- and Heterometallic Complexes Constructed from Hexafluoroacetylacetonato and Schiff Base Complexes as Building-Blocks, Mihaela Mocanu, Sergiu Shova, Francesc Lloret, Miguel Julve, Marius Andruh, A XXXV-a Conferință Națională de Chimie, 2-5 Octombrie 2018, Căciulata, prezentare orala.

Dissemination of Results - 2018

Conferences

8. Strategie originală de sinteză conducând la complcși heterotrispin *2p-3d-4f*, Andrei A. Pătrașcu, Marius Andruh, Sesiune de Comunicări Științifice Studențești, București, 25 mai 2018, prezentare orala.

9. Novel Heterotrispin Complexes, Andrei A. Pătrașcu, Marius Andruh, A XXXV-a Conferință Națională de Chimie, Căciulata, România, 2-5 Octombrie 2018, prezentare orala.

10. Noi complecși Heterotrispin, Andrei A. Pătrașcu, Marius Andruh, Conferința Națională a Școlilor Doctorale din Consorțiul Universitaria, Ediția I, Iași, 31 octombrie – 3 noiembrie 2018, prezentare orala.

Dissemination of Results - 2018

POSTER

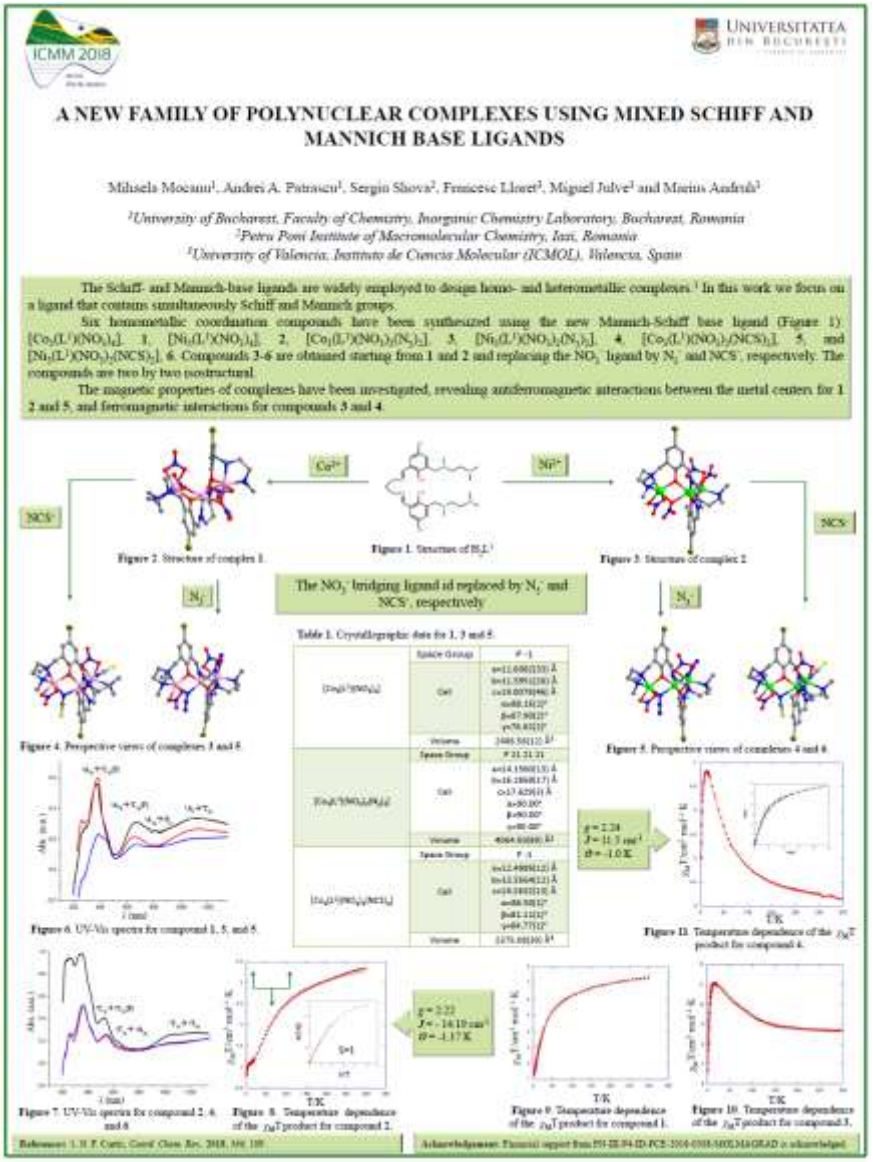
A new family of polynuclear complexes using mixed Schiff and Mannich base ligands,

Mihaela Mocanu, Andrei A. Patrascu, Francisco Lloret, Miguel Julve, Marius Andruh,

16th International Conference on Molecular-Based Magnets

Rio de Janeiro, Brazil

1-5 September 2018



Dissemination of Results - 2018

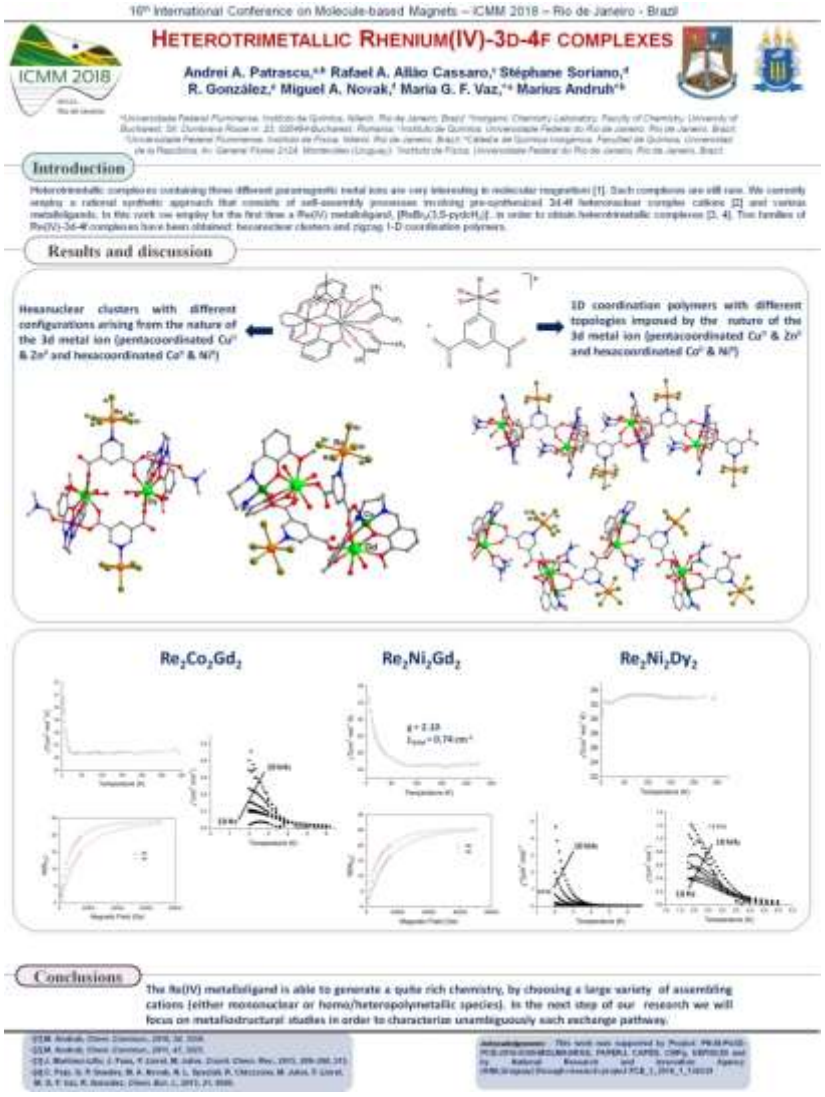
POSTER

Heterotrimetallic Rhenium(IV)-3*d*-4*f* complexes

Andrei A. Patrascu, Rafael A. Allão Cassaro, Stéphane Soriano, Ricardo González, Miguel A. Novak, Maria G. F. Vaz, Marius Andruh

16th International Conference on Molecule-based Magnets – ICMM 2018

Rio de Janeiro, Brazilia
1-5 September 2018



Dissemination of Results - 2019

Autori: Andrei A. Patrascu, Matteo Briganti, Stephane Soriano, Sergiu Calancea, Rafael A. Allao-Cassaro, Federico Totti, Maria G.F. Vaz, Andruh Marius

Titlul articolului: *SMM behavior tuned by an exchange coupling LEGO® approach for chimeric compounds: First 2p-3d-4f hetero-tri-spin complexes with different metal ions bridged by one aminoxyl group*

Inorg. Chem., 2019, doi.org/10.1021/acs.inorgchem.9b01998

■ ACKNOWLEDGMENTS

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Inorganic Chemistry

Article

SMM Behavior Tuned by an Exchange Coupling LEGO Approach for Chimeric Compounds: First 2p−3d−4f Heterotrispin Complexes with Different Metal Ions Bridged by One Aminoxyl Group

Andrei A. Patrascu,[†] Matteo Briganti,[‡,*] Stéphane Soriano,[§] Sergiu Calancea,[†,∥] Rafael A. Allão Cassaro,[⊥] Federico Totti,[‡,#] Maria G. F. Vaz,[⊥,*] and Marius Andruh[†,*]

[†]Inorganic Chemistry Laboratory, Faculty of Chemistry, University of Bucharest, Str. Dumbrava Roșie nr. 23, 020464-Bucharest, Romania

[‡]Department of Chemistry "Ugo Schiff" and INSTM RU University of Florence, 50019 Sesto Fiorentino, Italy

[§]Instituto de Física, Universidade Federal Fluminense, 24210-346-Niterói, Rio de Janeiro, Brazil

[∥]Faculty of Chemistry and Chemical Technology, Moldova State University, MD-2009-Chisinau, Moldova

[⊥]Instituto de Química, Universidade Federal do Rio de Janeiro, 21941-909-Rio de Janeiro, Brazil

[#]Instituto de Química, Universidade Federal Fluminense, 24020-346-Niterói, Rio de Janeiro, Brazil

Supporting Information

ABSTRACT: Coordination compounds containing three different spin carriers (2p, 3d, and 4f), with the general formula $[M^{II}Dy^{III}(LH)(hfac)_5]$ (M = Co, Ni, Mn, Zn), have been obtained using Mannich ligands decorated with a nitronyl−nitroxide fragment. The synthetic approach is general and leads to binuclear 3d−4f complexes, the two metal ions being bridged by one aminoxyl group and by one oxygen atom arising from a $hfac^-$ ligand. Triangular spin topology affords significant 2p−3d, 3d−4f, and 2p−4f exchange interactions. For the $[Co^{II}Dy^{III}Rad]$ derivative obtained using a nitronyl−nitroxide chiral ligand, a high energy barrier (~200 cm^{-1}) and a slow relaxation behavior below 30 K were found and rationalized by ab initio calculations. The improvement of magnetic properties comes from the synergy of optimal single ions properties and exchange couplings contributions where the Co^{II}−Rad interaction becomes the leading one. The role played by this interaction is clearly proved by the investigation of the magnetic properties of the $[Zn^{II}Dy^{III}Rad]$ derivative, with a much lower energy barrier (12.7 cm^{-1}) and by the lack of SMM behavior of the previously reported $[Co^{II}Dy^{III}Rad]$ compound (*Chem. Commun.* 2017, *53*, 6504), with a linear topology of spin carriers and a negligible Co^{II}−Rad interaction.

■ INTRODUCTION

The combination of different spin carriers is a valuable synthetic strategy to obtain molecular magnetic materials. Indeed, most of the 3-D molecule-based magnets[1] and single chain magnets (SCMs),[2] as well as numerous single molecule magnets (SMMs)[3] are 3d−rad, rad−4f, 2p−rad, and 2p−4f heterobispin complexes. Particular pairs of spin carriers are chosen in order to afford large spin values of the ground state with a large magnetic anisotropy (especially for SMMs and SCMs) and, hopefully, to add an exchange coupling interaction acting as an effective field on the metal/rare earth ion(s) and, therefore, able to overcome the fast relaxation shortcomings derived by the quantum tunneling process. Consequently, the spin has a zero probability to reach the other side of the double well potential by tunneling through the anisotropy barrier and needs to thermally overcome it. As far as the heterotrispin systems are concerned, they are less numerous. Such compounds contain either three different paramagnetic ions,[4] or two different paramagnetic ions and an organic radical (2p).[5] The first complexes constructed from two different 3d metal ions and nitronyl−nitroxide or imino−nitroxide radicals have been reported by Kahn et al.,[6] Mallah et al.,[7] and by Verdaguer et al.[8] Several years later, one of us described the first 2p−3d−4f complex, constructed from trinuclear $[Cu^{II}_2Gd^{III}]$ cationic units connected by $TCNQ^{\bullet-}$ anionic radicals.[9] Although formally a 2p−3d−4f system, this complex behaves, from the magnetic point of view, like a heterobimetallic $[Cu^{II}Gd^{III}]$ system, since the strong π−π stacking interactions between the $TCNQ^{\bullet-}$ radicals lead, even at room temperature, to diamagnetic supramolecular dimers. To design 2p−3d−4f heterotrispin complexes, in which the 2p spin

Received: July 5, 2019

Dissemination of Results - 2019

POSTER

2p-3d-4f heterotrispin complexes with different metal ions bridged by one aminoxyl group

Andrei A. Pătrașcu, Stéphane Soriano, Maria G.F. Vaz, Marius Andruh

21st Romanian International Conference on Chemistry and Chemical Engineering – RICCCE21

Mamaia, Constanţa, ROMANIA
4 - 7 September 2019