UNIVERSITATEA DIN BUCUREȘTI

VIRTUTE ET SAPIENTIA

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

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

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Project Team

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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.

Dissemination of Results

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*

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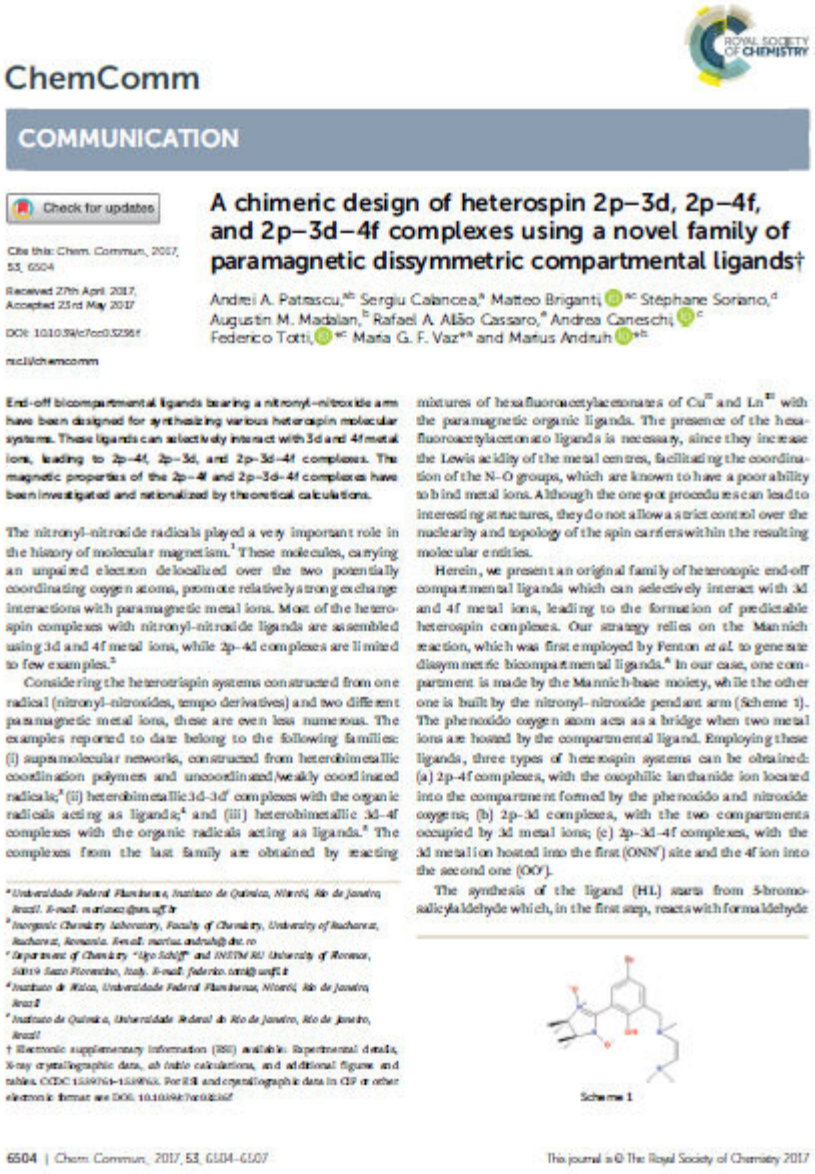

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A chimeric design of heterospin 2p–3d, 2p–4f, and 2p–3d–4f complexes using a novel family of paramagnetic dissymmetric compartmental ligands†

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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 heterospin 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

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† Electronic supplementary information (ESI) available: Experimental details, X-ray crystallographic data, *ab initio* calculations, and additional figures and tables. CCDC 1539763–1539765. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7cc03256f

Dissemination of Results

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).