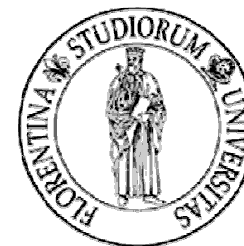




Universitatea din Bucuresti



**Università degli studi
Firenze**

Multifunctional Molecular Nano-systems

Project 644/07.01.2013

Timespan: 2013 – 2014 (24 months)

Project financed by:



Summary & Objectives

The project seeks to combine the principles of supramolecular chemistry with crystal engineering approaches to obtain compounds of interest in materials science, with a special focus on magnetic and luminescent properties. The project has also a fundamental component aiming to enlarge our knowledge and experience in metallosupramolecular chemistry and crystal engineering finalized with the production of multifunctional molecular systems.

Two families of molecular compounds will be synthesized and studied, using similar organic ligands: (i) discrete multimetallic species; (ii) coordination polymers. We intend to design low-dimensional heterometallic complexes (clusters and 1-D polymers), in order to obtain luminescent Single Molecule Magnets (SMMs) and Single Chain Magnets (SCMs).

Among the scientific objectives, an important goal is the training of young researchers and the transfer of knowledge between the two laboratories. Both of them have recognized expertise, which is complementary with the partner's, and are interested in transferring the knowledge, meaning synthetic strategies from the Romanian to the Italian part, exchanging with magnetic and electronic characterisation the other way around.

Partners

Team 1 – University of Bucharest, Faculty of Chemistry

Romanian Coordinator of the Project: Acad. Marius Andruh

Team 2 – Università degli studi di Firenze

Italian Coordinator of the Project: Prof. Andrea Caneschi

Project Teams

Team 1 Members:

Dr. Ruxandra Gheorghe
Dr. Augustin Madalan
Dr. Alina Dinca
Dr. Adrian Ion
Dr. Maria Alexandru

Team 2 Members:

Prof. Roberta Sessoli
Dr. Lorenzo Sorace
Dr. Giordano Poneti
Prof. Andrea Dei
Dr. Maria Fittipaldi
Dr. Federico Totti
Dr. Cristiano Benelli

Project Budget – Romanian Team

No.	BUDGET CHAPTER	2013 (lei)	2014 (lei)	TOTAL (lei)
1	MOBILITY	6149,61	9676,82	15 826,43
	TOTAL BUDGET	6149,61	9676,82	15 826,43

Results:

“Magnetic and Luminescent Binuclear Double-Stranded Helicates” *Inorg. Chem.* **2014**, *53*, 7738

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Magnetic and Luminescent Binuclear Double-Stranded Helicates

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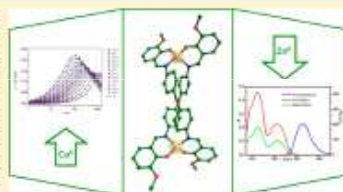
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Supporting Information

ABSTRACT: Three new binuclear helicates, $[M_2L_2] \cdot 3DMF$ ($M = Co(II)$, 1; $Zn(II)$, 3) and $[Cu_2L_2] \cdot DMF \cdot 0.4H_2O$ (2), have been assembled using the helicate H₂L that results from the 2:1 condensation reaction between *o*-vanillin and 4,4'-diaminodiphenyl ether. The metal ions within the binuclear helicates are tetra-coordinated with a distorted tetrahedral geometry. Direct current magnetic characterization and EPR spectroscopy of the $Co(II)$ derivative point to an easy axis type anisotropy for both $Co(II)$ centers, with a separation of at least 55 K between the two doubles. Dynamic susceptibility measurements evidence slow relaxation of the magnetization in an applied dc field. Since the distance between the cobalt ions is quite large (11.59 Å), this is attributed in a first instance to the intrinsic properties of each $Co(II)$ center (single-ion magnet behavior). However, the temperature dependence of the relaxation rate and the absence of slow dynamics in the $Zn(II)$ -doped sample suggest that neither the simple Orbach mechanism nor Raman or direct processes can account for the relaxation, and collective phenomena have to be involved for the observed behavior. Finally, due to the rigidification of the two organic ligands upon coordination, the pure zinc derivative exhibits fluorescence emission in solution, which was analyzed in terms of fluorescence quantum yield and lifetime.



INTRODUCTION

The rational design of metallic helicates represents one of the early spectacular achievements of metallo-supramolecular chemistry.¹ Several classes of organic molecules (helicates) were synthesized and used for the assembly of double- and triple-stranded homo- and heterometallic helicates, which have been recently reviewed in excellent papers.² The helicates are linear strands with repeating complexation sites separated by suitable spacers.³ Numerous helicates are *bi*-Schiff bases derived from hydrazine (diamine ligands)⁴ or long/rigid diamines.^{5,6} Among the acyclic helicates, which are related to the present work, we mention the Schiff bases resulting from the 2:1 condensation between *o*-vanillin and various diamines.⁷

Apart from their beauty, the metalhelicates display exciting physical properties, such as luminescence and magnetism. There are two important types of luminescent helicates: those for which the light emission arises from the metallic centers (most frequently lanthanide cations),⁸ and helicates owing their

luminescence to the organic ligand, which becomes rigid upon coordination to the metal ions (for example $Zn(II)$ ions).⁹ From the magnetic point of view, the metal ions within a helical structure can interact with each other, when the distance between them is small and the bridging fragments are able to mediate the exchange interactions. If the metal ions are significantly separated, they behave independently from the magnetic point of view. In this last case two types of magnetic behavior are particularly important: (i) the metal ions exhibit spin crossover phenomena;¹⁰ (ii) each metal ion shows slow relaxation of the magnetization; that is, it acts as a single-ion magnet (SIM).¹¹ Most of the helicates featuring SIM behavior are based on strongly anisotropic lanthanide cations. In this paper we report on three new binuclear helicates constructed using a Schiff-base helicate resulting from the condensation of *o*-vanillin with 4,4'-diaminodiphenyl ether. This organic

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DEDICATION

This paper is dedicated to our friend, Professor Miguel A. Novak, on the occasion of his 60th birthday.

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- (1) (a) Constable, E. C. *Chem. Ind.* **1994**, 56. (b) Constable, E. C. In Lehn, J.-M.; Atwood, L. Davis, J. E. D.; MacNicol, D. D.; Vögtle, F., Eds. *Comprehensive Supramolecular Chemistry*; Oxford: Pergamon, 1996; Vol. 9, p 213. (c) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (d) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022. (e) Lehn, J.-M. *Supramolecular Chemistry—Concepts and Perspectives*; VCH: Weinheim, 1995.