

Paramagnetic polyoxometalates (POMs) as metalloligands for constructing heterotrispin complexes

PN-III-P1-1.1-TE-2016-1633 (nr. 1/2018)

Financial support: UEFISCDI

Project team:

Project leader: dr. Catalin Maxim

Members:

dr. Silviu Nastase

dr. Cristian D. Ene

student Dragos Negreanu

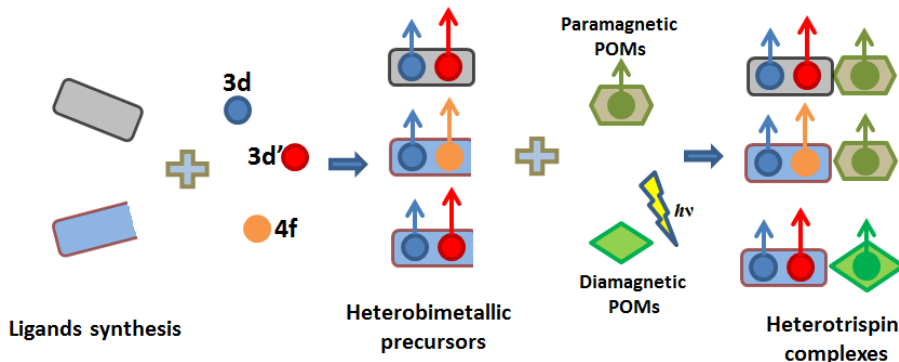
student Alexandru Topor

Abstract:

The present project will concentrate on the development the synthesis and characterization of new molecular heterotrispin systems based on heterobimetallic 3d-3d' and 3d-4f precursors and paramagnetic polyoxometalates(POMs) as metalloligands by using the molecular approach strategy. This strategy focuses on POMs as ligands, and will be used for the first time in heterotrispin chemistry.

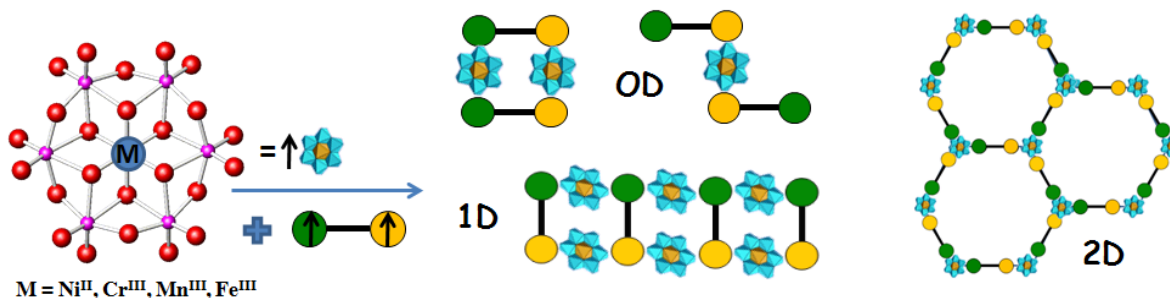
Two synthetic routes will be followed to achieve the envisaged heterotrispin networks:

- the self-assembly process involving heterobinuclear cationic complexes and paramagnetic polyoxometalates
 - as a follow up of the self-assembly route, the photo-generation of the trispin complexes by photoinduced intramolecular charge transfer in POMs based organic-inorganic hybrids.
- New organic ligands will be synthesized in order to design new heterodinuclear precursors with easily accessible positions that favor strong interaction and flexible coordination spheres.



Objectives:

- A. *Design, synthesis and characterization of new bicompartamental Schiff base ligands (macrocyclic or side-off type).*
- B. *Design, synthesis and characterization of new heterobimetallic 3d-3d' and 3d-4f complexes to be further used as nodes.*
- C. *Design, synthesis and characterization of new heterotrispin complexes containing paramagnetic POMs as metalloligands.*
- D. *Magneto-structural correlations in heterometallic complexes.*



Dissemination of results 2018:

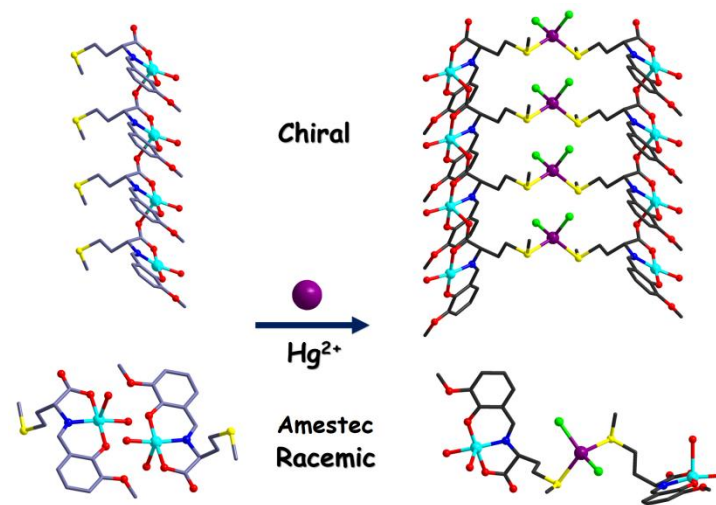
Conferences:

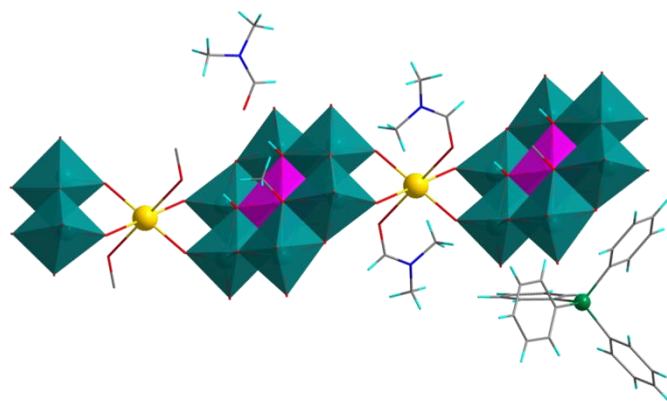
- Catalin Maxim, Cristian D. ENE, Marius Andruh, *Chiral coordination polymers containing tridentate Schiff bases ligands. Crystal structures, optical and magnetic properties*, **68th Conference of Japan Society of Coordination Chemistry** (JSCC), July 28-30, 2018, Sendai, Japan, (oral presentation)
- Cristian D. Ene, Catalin Maxim, Rodolphe Clérac, Narcis Avarvari, Marius Andruh, *Enantiopure versus racemic mixture in reversible, two-step, single-crystal-to-single-crystal transformations of copper(II) complexes, accompanied by drastic changes of the magnetic properties*, **43rd International Conference on Coordination Chemistry** (ICCC2018), July 30 -August 4, 2018 , Sendai, Japan, (oral presentation)

Conferences:

- **Chirality driven single-crystal-to-single-crystal transformations of copper(II) coordination polymers**, Catalin Maxim, Cristian D. Ene, Marius Andruh, 9th International Conference of the Chemical Societies of the South-East European Countries (ICOSECS9), Targoviste, 8-11 mai 2019, prezentare orală.
- **On the role played by the chirality of ligands on the aggregation of heterometallic Cu^{II}-Hg^{II} complexes**, Catalin Maxim, Marius Andruh, 21st Romanian International Conference on Chemistry and Chemical Engineering (RICCCE2019), Constanta, 4-7 Septembrie 2019 Romania, keynote lecturer.
- **Synthesis and characterization of three new asymmetric binuclear Schiff-base 3d-4f compounds** Catalin Maxim, Alexandru Topor, Marius Andruh, 9th International Conference of the Chemical Societies of the South-East European Countries (ICOSECS9), Targoviste, 8-11 mai 2019, poster.
- **Constructing heterotrispin systems by employing Anderson polyoxoanions**, Catalin Maxim, Cristian D. Ene, Diana Trandafir, Dragos Negreanu, 21st Romanian International Conference on Chemistry and Chemical Engineering (RICCCE2019), Constanta, 4-7 Septembrie 2019 Romania, poster.

Paper: (2019) Chirality, 31 (9), pp. 621-627





Transmission electron microscopy in life sciences Theoretical and practical course -November 2019

Catalin Maxim
Cristian Dumitru Ene

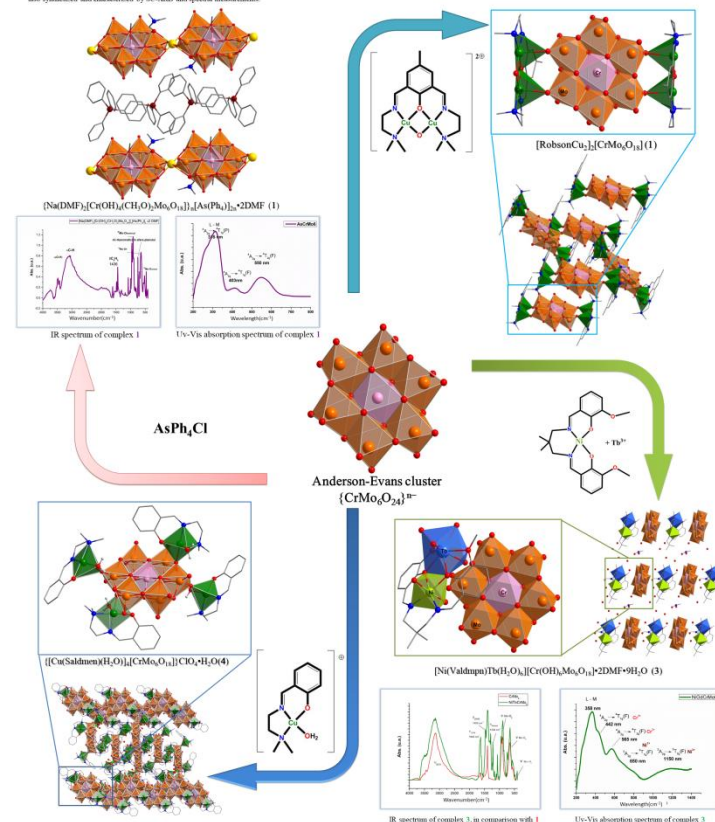


Constructing heterotriscip systems by employing Anderson polyoxoanions

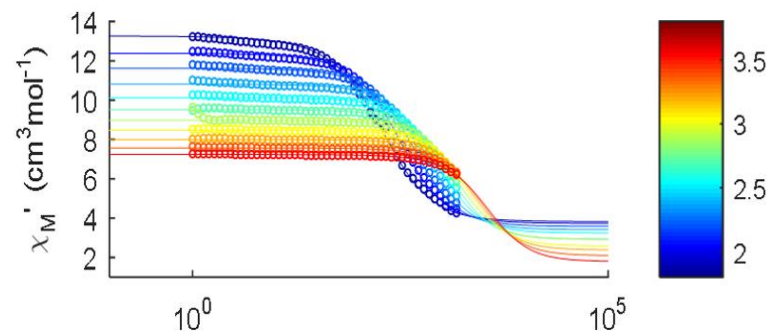
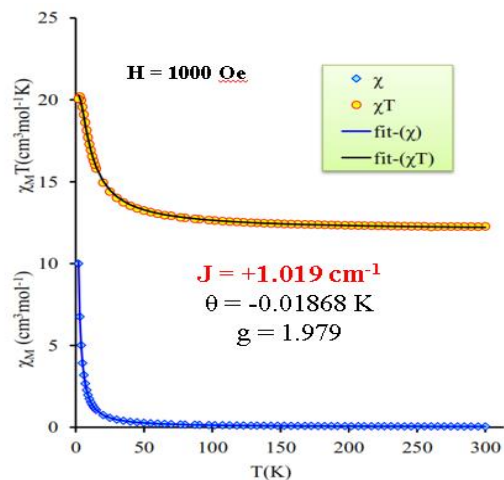
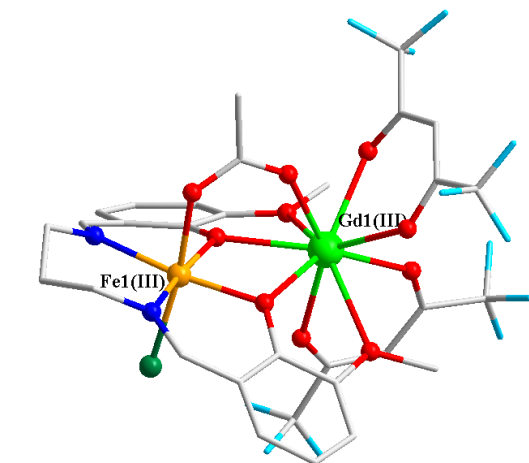
Cristian D. Ene¹, Dragos Negreanu¹, Diana Trandafir¹, Catalin Maxim¹

¹ "Ilie Murgulescu" Institute of Physical Chemistry, Romanian Academy, University of Bucharest, Faculty of Chemistry, Inorganic Chemistry Laboratory, 2b, Dabulovici Road nr. 23, 020464 Bucharest, Romania

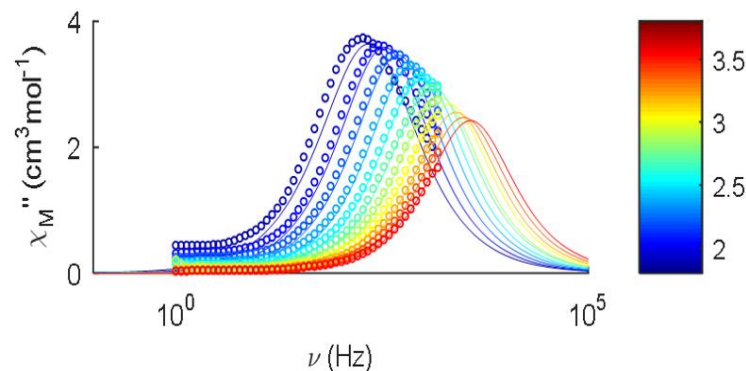
Abstract: Organic-inorganic molecular architectures based on polyoxometalates (POMs) are increasingly investigated for their peculiar structures and properties with potential applications in fields of catalysis, luminescence, and magnetism. Apart from being stable molecules that preserve their structure in solid state and on surfaces, POMs can both accommodate other magnetic ions and be subjected to redox reactions, leading to mixed-valence isoforms. These features make them appealing candidates for obtaining heterotriscip systems, a scarcely investigated class of magnetic compounds. POMs consist of various anionic polyoxoclate clusters based on a certain number of octahedral units containing metal and oxygen atoms which share edges and corners to form a specific core. This core can display different shapes and sizes, the most common being Keggin, Lindqvist, and Anderson-type anions. The last one mentioned is made of six (3006) octahedral fragments sharing only edges which generate a hexagon-like structure with the central cavity housing a heterometal ion. In one case, the scaffold and the guest metal ions are Mo(VI) and Cr(III), respectively. The resulting Anderson polyoxometalate is preserved and readily available as building block in the form of a new compound, (APh₃)₃[Cr(OH)₄Cr₂O₇(OH)₂Na(DMF)₃·2DMF, whose structure and physico-chemical behavior are presented herein. Derivatives that contain this anion and complex cations (homoe and heterotriscip systems) were also synthesized and characterized by SC-XRD and spectral measurements.



Acknowledgements. Financial support from the UEFISCDI (Project PN-III-P1-1.1-TE-2016-1633) is gratefully acknowledged.



FeDy



Dissemination of results 2020:

Paper: (2020) One-dimensional coordination polymers constructed from copper(II) ions and chromato bridges: Synthesis, crystal structures and thermal analysis

[Inorganica Chimica Acta](#) 509, 119663