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**P4 – Fundamental and Frontier Research
Exploratory Research Project (PCE),
PN-III-P4-ID-PCE-2016-0321
Contract no. 88/2017**

**NEW VERSATILE DICYANIDOMETALLATE PRECURSORS
[M^{III}(L)(CN)₂]⁻ FOR DESIGNING HETEROMETALLIC
MOLECULAR MAGNETIC MATERIALS**

Director: Dr. Gabriela MARINESCU

12.07.2017 – 31.12.2019

Summary

The present project develops a systematic study on the design and synthesis of new versatile dicyanidometallate $[M^{III}(L)(CN)_2]^-$ precursors ($M^{III} = Cr, Ru$ and Os , L = compartmental ligands of Schiff base type, derived from condensation reaction between salicylaldehyde or *o*-vanillin with various diamines, including chiral amines) and the investigation of the possibility to use them as tectons for the construction of cyanido-bridged heterometallic complexes with novel topologies, structural diversity, and predictable magnetic properties.

The synthetic approach towards heteropolymetallic systems consists in self-assembly processes between the $[M^{III}(L)(CN)_2]^-$ tectons and solvated metal ions, partially blocked complexes (e.g. mononuclear 3d complexes or binuclear 3d-3d', 3d-4f complexes) or alkoxo bridged homo- and heterometallic cationic clusters. The binuclear complexes 3d-3d', 3d-4f with compartmental ligands, due to their versatility and structural flexibility, efficiently act as tectons in designing heterotrimetallic systems with relevance in molecular magnetism. A special emphasis will be given to the synthesis of 3d-3d', 3d-4(5)d, 3d-4f, 4(5)d-4f or 3d-4f-4(5)d, 3d-3d'-4d heterometallic systems. In order to obtain systems with improved single-molecule magnets (SMM) or single-chain magnets (SCM) behavior, the metal ions with large magnetic anisotropy (Mn^{3+} , Co^{2+} , Ni^{2+} , Tb^{3+} , Dy^{3+} , Ho^{3+}) will be used. Another important objective of the project is focused on the use of chiral multidentate ligands for the obtaining of magneto-chiral systems, very interesting in the field of materials science.

From the fundamental point of view, our project will enrich the still poor coordination chemistry based on Ru^{III} , Os^{III} and Cr^{III} dicyanido tectons with novel examples. Besides aesthetic and structural diversity, the systems that will be obtained in this project are very important for understanding and interpreting their properties.

Main objectives

- Design and synthesis of new metalloligands $[M^{III}(L)(CN)_2]^-$ ($M^{III} = Cr, Ru$ and Os);
- The employment of these new metalloligands in assembling heterometallic complexes (discrete or infinite structures);
- Investigation of the magnetic properties of newly synthesized compounds;
- Magneto-structural correlations for the systems containing different paramagnetic (*e.g.* 3d-3d', 3d-4(5)d, 3d-4f, 4(5)d-4f or 3d-3d'-4(5)d, 3d-4f-4(5)d) centers across different bridges.

Research team

1. Marinescu Gabriela	Scientific Researcher, CS I	Experienced researcher Director of the project
2. Culita Daniela Cristina	Scientific Researcher, CS II	Experienced researcher Team member
3. Lete Cecilia	Scientific Researcher, CS II	Experienced researcher Team member
4. Maxim Catalin	University assistant	Experienced researcher Team member
5. Tudor Violeta	Associate professor	Experienced researcher Team member
6. Dogaru Andreea Georgeta	Research assistant	Postdoctoral researcher Team member
7. Negreanu Dragos Gabriel	Master student	Masterand Team member
8. Nica Simona Filofteia	Scientific Researcher, CS II	Experienced researcher Team member

Budget

Year	Finance (lei)		Total (lei)
	Budget	Credit	
2017	178602	76544	255146
2018	296065	0	296065
2019	298789	0	298789
Total	773456	76544	850000

Dissemination of Results

Conferences presentations:

G. Marinescu, C. Maxim, A.M. Madalan, S. Shova, R. Clérac, M. Andruh, *[Ru^{III}(valen)(CN)₂]: a New Building Block to Design 4d-3d/4d-4f Heterometallic Complexes*, **VI European conference on Molecular Magnetism, August 27-31, 2017, Bucharest, Romania.**

V. Tudor, C. Maxim, A. Tanase, A. Topor, R. Poenaru, D. Hiuhiu, F. Lloret, M. Julve and M. Andruh, *Homo and heterometallic clusters of V(IV), Mn(II/III), Co(II/III)/Cu(II), Co(II/III)/Mn(II/III), Co(II/III)/Fe(III) with aminoalcohols and carboxylic acids: synthesis, crystal structures and magnetic properties*, **VI European conference on Molecular Magnetism, August 27-31, 2017, Bucharest, Romania.**

G.D. Negreanu, N. Stanica, M. Catalin, G. Marinescu, *New dicyanoruthenium(III) building blocks for obtaining heterometallic complexes*, **15th International Conference “Students for Students”, 18-22 April, 2018, Cluj-Napoca, Romania.**

G. Marinescu, C. Maxim, A.M. Madalan, S. Shova, R. Clérac, M. Andruh, *Ru^{III}-M^{II} heterobimetallic coordination polymers. Synthesis, crystal structures, and magnetic properties*, **Congress SCF 18, 02-04 July, 2018, Montpellier, France.**

V. Tudor, C. Maxim, A. Apostol, A. Tanase, A. Topor, R. Poenaru, D. Hiuhiu, A.C. Sebe, F. Lloret, M. Julve, M. Andruh, *Homo and heterometallic clusters of V^{IV} , Mn^{II}/Mn^{III} , Co^{II}/Co^{III} , $Co^{II/III}/Cu^{II}$, $Co^{II/III}/Mn^{II/III}$, $Co^{II/III}/Fe^{III}$, $Co^{II/III}/Zn^{II}$, $Co^{II/III}/Ni^{II}$ with Aminoalcohols and Carboxylic Acids: Synthesis, Crystal Structures and Magnetic Properties*, **43rd International Conference on Coordination Chemistry (ICCC 2018), July 30 – August 04, 2018, Sendai, Japan.**

A.G. Dogaru, G. Marinescu, C. Maxim, R. Clérac, M. Andruh, *3d-5d-4f Heterometallic Octanuclear Complexes and 1D Coordination Polymers Assembled From The Same Lego Pieces*, **International Conference RICCE XXI, 4-7 September 2019, Mamaia, Romania.**

M.Sc.

Dragos Gabriel Negreanu

Topic of thesis "*Ruthenium(III) complexes as building blocks in designing molecular magnets*"

Defended on June 28, 2019

University of Bucharest, Faculty of Chemistry, Inorganic Chemistry Laboratory

Papers:

Dicyanido Ru(III) complexes: synthesis and crystal structures, D.G. Negreanu, D.C. Culita, C. Maxim, S. Shova, G. Marinescu, M. Andruh, *Rev. Roum. Chim.*, **2018**, 63(12), 1181-1189.

Synthesis, characterization and cytotoxic activity of Co(II), Ni(II), Cu(II), and Zn(II) complexes with nonsteroidal antiinflammatory drug isoxicam as ligand, D.C. Culita, L. Dyakova, G. Marinescu, T. Zhivkova, R. Spasov, L. Patron, R. Alexandrova, O. Oprea, *J. Inorg. Organomet. Polym. Mater.*, **2018**, 29, 580–591.

Heterometallic 3d-4d coordination polymers assembled from trans-[Ru^{III}(L)(CN)₂]⁺ tectons and 3d cations, G. Marinescu, A.M. Madalan, C. Maxim, S. Shova, R. Clérac, M. Andruh, *Dalton Trans.*, **2019**, 48, 15455–15464.

Assembling {Cu^{II}Ln^{III}Os^{III}} heterotrimetallic octanuclear complexes and 1D coordination polymers from the same molecular modules, A. Dogaru, J.-L. Liu, C. Maxim, G. Marinescu, R. Clérac, M. Andruh, *Polyhedron*, **2019**, <https://doi.org/10.1016/j.poly.2019.114242>.

Heteroleptic Ru(III) complexes immobilized on SBA-15 mesoporous, silica as highly potent antimicrobial and cytotoxic agents, D.C. Culita, G. Marinescu, C. Romanitan, S. Somacescu, C.D Ene, V. Marinescu, M. Popa, L. Marutescu, M. Stan, C. Chifiriuc, *submitted to Microporous & Mesoporous Materials*, **2019**, under review.

Single-crystal to single-crystal thermal transformations in discrete tetrameric chromium(III) complexes, (provisional title) D.C. Culita, C. Maxim, C. Ene, T. Mocanu, C. Romanitan, G. Marinescu, M. Andruh, in progress.