Universitatea din Bucuresti

Institut des Sciences Chimiques de Rennes

CRYSTAL ENGINEERING OF MULTIFUNCTIONAL MOLECULE-BASED MATERIALS

PN-II-ID-JRP-RO-FR-2011-2-0034 (12/2013)

Timespan: 2013 – 2016

Project financed by:

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

Agence Nationale de la Recherche
ANR

Centre de Recherche Paul Pascal Bordeaux

Institut des Sciences et Technologies Moléculaires d’ Angers

Summary

The current project addresses fundamental issues for the understanding of important questions faced today by researchers in Molecular Magnetism, particularly the control and the manipulation of magnetic coupling and magnetic anisotropy on the other hand. Their combined role will be particularly investigated here in a variety of coordination complexes developed in Bucharest, which exhibit Single Molecule Magnet (SMM), Single Chain Magnet (SCM), Magneto-Caloric Effect (MCE) or PhotoMagnetic properties, together with their introduction in molecular conductors.

Our collaborative consortium associates one research group in Bucharest (M. Andruh), and one research group in Bordeaux (R. Clérac, C. Mathonière), both with a strong experience in molecular magnetism and coordination chemistry of classical ($S > \frac{1}{2}$), anisotropic spins, together with two research groups in Rennes (M. Fourmigué) and Angers (N. Avarvari), with a strong background in molecular conductors and quantum ($S = \frac{1}{2}$) spin systems, and crystal engineering strategies. The Bucharest group is internationally recognized for the preparation of very original magnetic coordination compounds. This project is devoted to adding new functions to these compounds as magnet-like behaviour, photomagnetic or conducting properties. The three French partners offer complementary expertise along these lines to develop these series of complexes designed and prepared in Bucharest.

Objectives

The main objective of the project is to synthesize and characterize molecular magnetic materials displaying specific physical properties, like spin crossover or photomagnetism, which would allow to write information on a magnetic state using another stimulus than the magnetic field (light, pressure, temperature…).

1. Synthesis of novel magnetic materials: control of magnetic coupling and/or anisotropy;

2. Elaboration of conducting materials: electron transfer processes in bimetallic complexes;

3. Advanced physical properties of the materials: possible association of nano-magnet or spin crossover behavior with metallic conductivity in multifunctional materials;

4. Organization of high level classes on molecular materials for Master and PhD students.

Partners

Team 1 – University of Bucharest, Faculty of Chemistry

Romanian Coordinator of the Project: Acad. Marius Andruh

Team 2 – Institut des Sciences Chimiques de Rennes

French Coordinator of the Project: Dr. Marc Fourmigué

Team 3 – Centre de Recherche Paul Pascal Bordeaux

Team 3 leader: Dr. Rodolphe Clérac

Team 4 – Institut des Sciences et Technologies Moléculaires d' Angers

Team 4 leader: Dr. Narcis Avarvari

Project Teams

Team 1 Members:

Dr. Violeta Tudor

Dr. Augustin M. Madalan

Dr. Ruxandra Gheorghe

Dr. Delia-Laura Popescu

Dr. Gabriela Marinescu

Dr. Adrian Ion

Drd. Andreea Dogaru

Drd. Andrei Patrascu

Team 2 Members:

Dr. Olivier Jeannin

Dr. Thierry Guizouarn

Team 3 Members:

Prof. Corinne Mathonière

Dr. Mathieu Rouzières

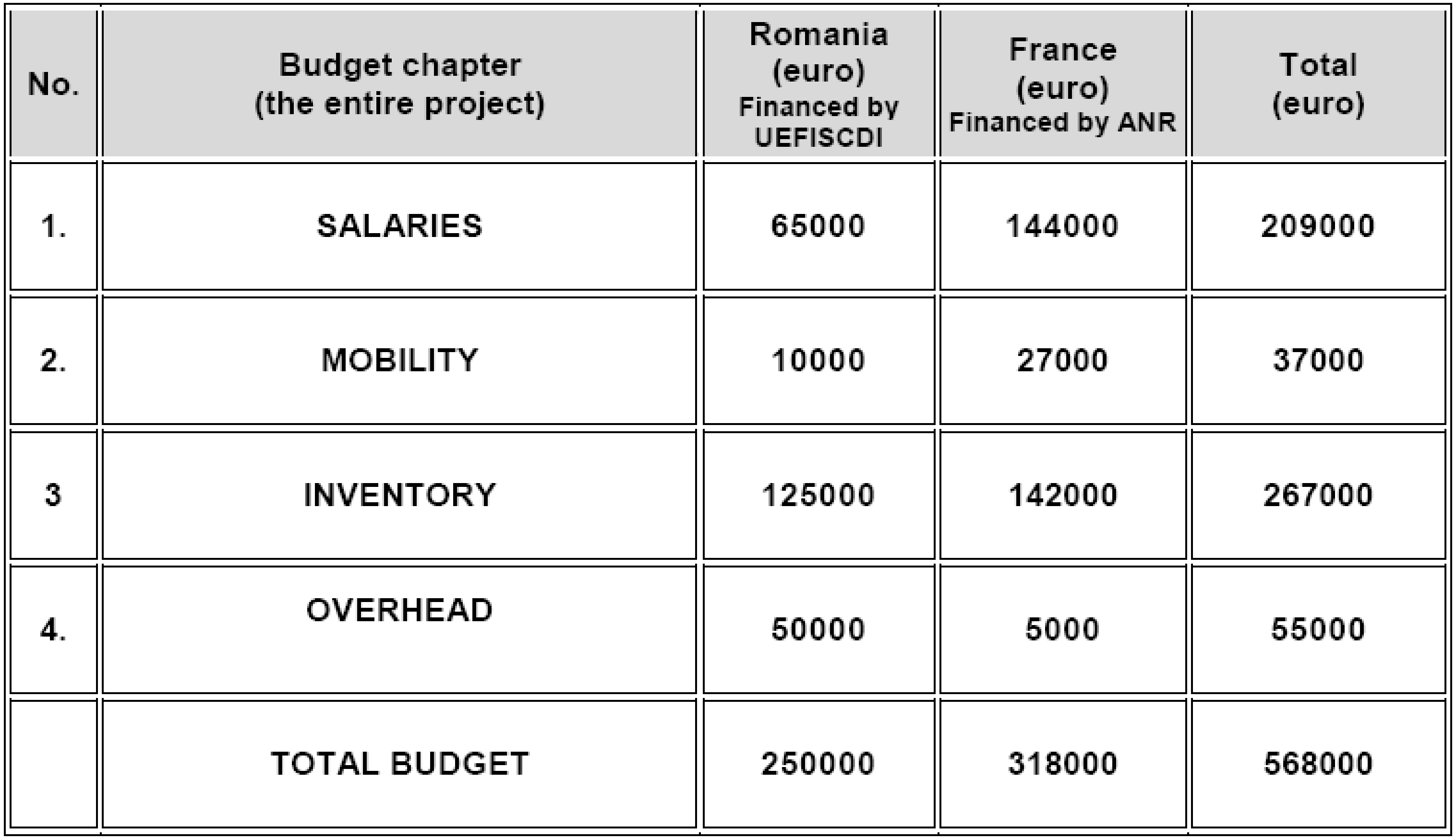
Team 4 Members:

Dr. Abdelkrim El-Ghayoury

Dr. Magali Allain

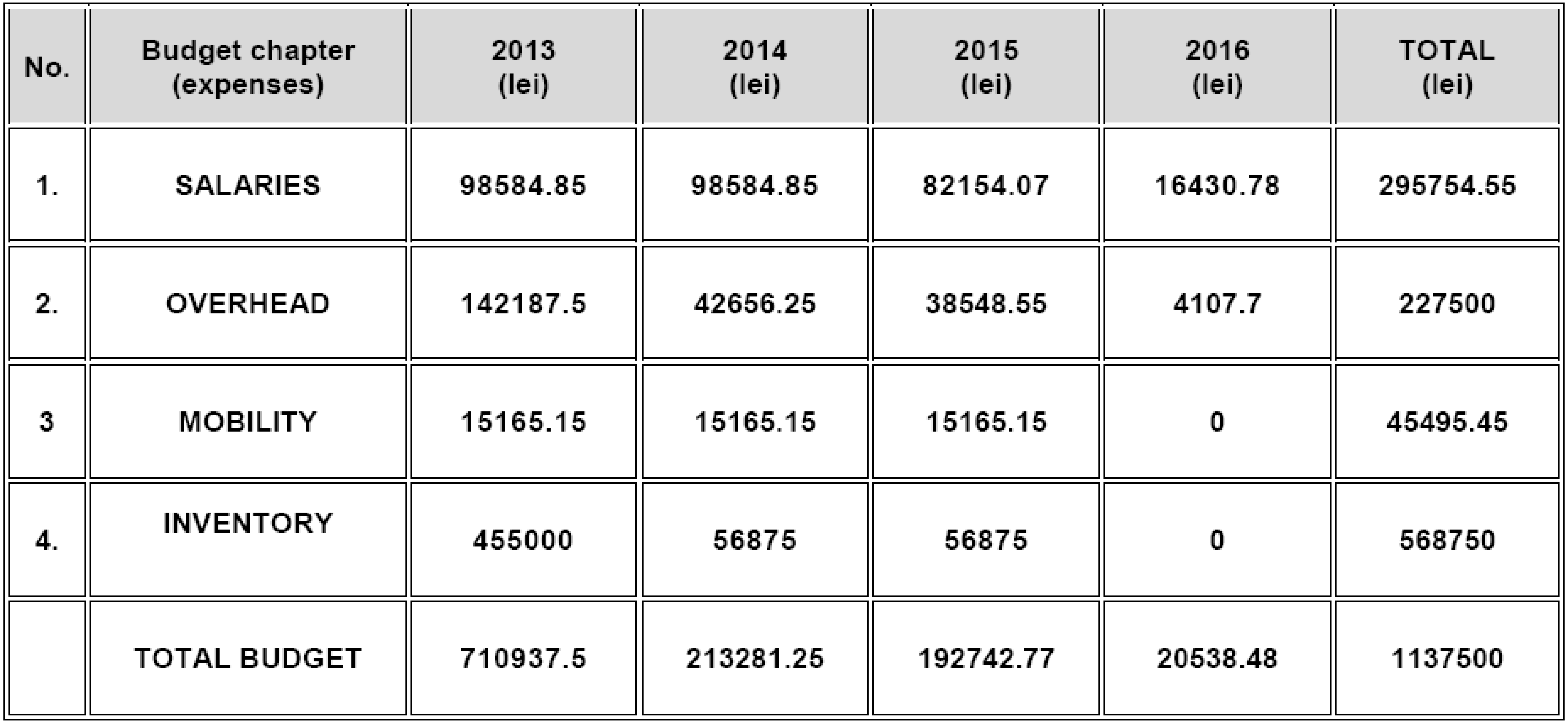
Dr. Thomas Cauchy

Project Budget



No.	Budget chapter (the entire project)	Romania (euro) Financed by UEFISCDI	France (euro) Financed by ANR	Total (euro)
1.	SALARIES	65000	144000	209000
2.	MOBILITY	10000	27000	37000
3	INVENTORY	125000	142000	267000
4.	OVERHEAD	50000	5000	55000
	TOTAL BUDGET	250000	318000	568000

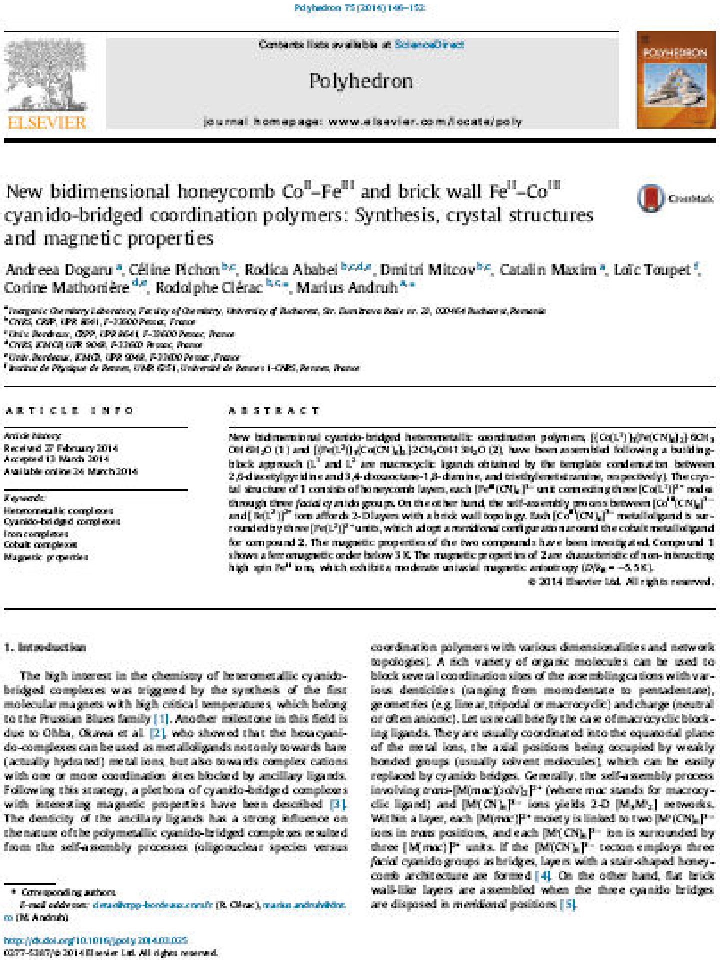
Project Budget – Romanian team



No.	Budget chapter (expenses)	2013 (lei)	2014 (lei)	2015 (lei)	2016 (lei)	TOTAL (lei)
1.	SALARIES	98584.85	98584.85	82154.07	16430.78	295754.55
2.	OVERHEAD	142187.5	42656.25	38548.55	4107.7	227500
3	MOBILITY	15165.15	15165.15	15165.15	0	45495.45
4.	INVENTORY	455000	56875	56875	0	568750
	TOTAL BUDGET	710937.5	213281.25	192742.77	20538.48	1137500

Dissemination of Results 2014

1. A. Dogaru, C. Pichon, R. Ababei, D. Mitcov, C. Maxim, L. Toupet, C. Mathonière, R. Clérac, M. Andruh, *New bidimensional honeycomb Co^{II}-Fe^{III} and brick wall Fe^{II}-Co^{III} cyanido-bridged coordination polymers: Synthesis, crystal structures and magnetic properties*, *Polyhedron* **2014**, *75*, 146-152.



Polyhedron 75 (2014) 146–152

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

New bidimensional honeycomb Co^{II}–Fe^{III} and brick wall Fe^{II}–Co^{III} cyanido-bridged coordination polymers: Synthesis, crystal structures and magnetic properties

Andreea Dogaru [a], Céline Pichon [b,c], Rodica Ababei [b,c,d,e], Dmitri Mitcov [b,c], Catalin Maxim [a], Loïc Toupet [f], Corine Mathonière [d,e], Rodolphe Clérac [b,c,*], Marius Andruh [a,*]

[a] Inorganic Chemistry Laboratory, Faculty of Chemistry, University of Bucharest, Str. Dumbrava Rosie nr. 23, 020464 Bucharest, Romania
[b] CNRS, CRPP, UPR 8641, F-33600 Pessac, France
[c] Univ. Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France
[d] CNRS, ICMCB, UPR 9048, F-33600 Pessac, France
[e] Univ. Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France
[f] Institut de Physique de Rennes, UMR 6251, Université de Rennes 1-CNRS, Rennes, France

ARTICLE INFO

Article history:
Received 27 February 2014
Accepted 13 March 2014
Available online 24 March 2014

Keywords:
Heterometallic complexes
Cyanido-bridged complexes
Iron complexes
Cobalt complexes
Magnetic properties

ABSTRACT

New bidimensional cyanido-bridged heterometallic coordination polymers, $[\{Co(L^1)\}_3\{Fe(CN)_6\}_2]\cdot 6CH_3OH\cdot 6H_2O$ (1) and $[\{Fe(L^2)\}_3\{Co(CN)_6\}_2]\cdot 2CH_3OH\cdot 3H_2O$ (2), have been assembled following a building-block approach (L^1 and L^2 are macrocyclic ligands obtained by the template condensation between 2,6-diacetylpyridine and 3,6-dioxaoctane-1,8-diamine, and triethylenetetramine, respectively). The crystal structure of 1 consists of honeycomb layers, each $[Fe^{III}(CN)_6]^{3-}$ unit connecting three $[Co(L^1)]^{2+}$ nodes through three *facial* cyanido groups. On the other hand, the self-assembly process between $[Co^{III}(CN)_6]^{3-}$ and $[Fe(L^2)]^{2+}$ ions affords 2-D layers with a brick wall topology. Each $[Co^{III}(CN)_6]^{3-}$ metalloligand is surrounded by three $[Fe(L^2)]^{2+}$ units, which adopt a meridional configuration around the cobalt metalloligand for compound 2. The magnetic properties of the two compounds have been investigated. Compound 1 shows a ferromagnetic order below 3 K. The magnetic properties of 2 are characteristic of non-interacting high spin Fe^{II} ions, which exhibit a moderate uniaxial magnetic anisotropy ($D/k_B = -5.5$ K).

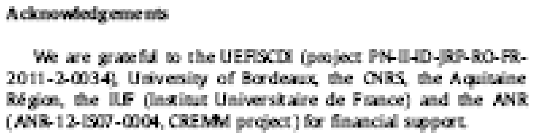
1. Introduction

The high interest in the chemistry of heterometallic cyanido-bridged complexes was triggered by the synthesis of the first molecular magnets with high critical temperatures, which belong to the Prussian Blues family [1]. Another milestone in this field is due to Ohba, Okawa et al. [2], who showed that the hexacyanido-complexes can be used as metalloligands not only towards bare (actually hydrated) metal ions, but also towards complex cations with one or more coordination sites blocked by ancillary ligands. Following this strategy, a plethora of cyanido-bridged complexes with interesting magnetic properties have been described [3]. The denticity of the ancillary ligands has a strong influence on the nature of the polymetallic cyanido-bridged complexes resulted from the self-assembly processes (oligonuclear species versus coordination polymers with various dimensionalities and network topologies). A rich variety of organic molecules can be used to block several coordination sites of the assembling cations with various denticities (ranging from monodentate to pentadentate), geometries (e.g. linear, tripodal or macrocyclic) and charge (neutral or often anionic). Let us recall briefly the case of macrocyclic blocking ligands. They are usually coordinated into the equatorial plane of the metal ions, the axial positions being occupied by weakly bonded groups (usually solvent molecules), which can be easily replaced by cyanido bridges. Generally, the self-assembly process involving *trans*-$[M(mac)(solv)_2]^{n+}$ (where mac stands for macrocyclic ligand) and $[M'(CN)_6]^{3-}$ ions yields 2-D $[M_3M'_2]$ networks. Within a layer, each $[M(mac)]^{n+}$ moiety is linked to two $[M'(CN)_6]^{3-}$ ions in *trans* positions, and each $[M'(CN)_6]^{3-}$ ion is surrounded by three $[M(mac)]^{n+}$ units. If the $[M'(CN)_6]^{3-}$ tecton employs three *facial* cyanido groups as bridges, layers with a stair-shaped honeycomb architecture are formed [4]. On the other hand, flat brick wall-like layers are assembled when the three cyanido bridges are disposed in meridional positions [5].

---

* Corresponding authors.
E-mail addresses: clerac@crpp-bordeaux.cnrs.fr (R. Clérac), marius.andruh@dnt.ro (M. Andruh).

http://dx.doi.org/10.1016/j.poly.2014.03.025



Acknowledgements

We are grateful to the UEFISCDI (project PN-II-ID-JRP-RO-FR-2011-2-0034), University of Bordeaux, the CNRS, the Aquitaine Région, the IUF (Institut Universitaire de France) and the ANR (ANR-12-IS07-0004, CREMM project) for financial support.

Dissemination of Results 2014

2. C. Maxim, D. G. Branzea, C. Tiseanu, M. Rouzières, R. Clérac, M. Andruh, N. Avarvari, *Cyanomethylene-bis(phosphonate) based lanthanides complexes: Structural, photophysical and magnetic investigations*, *Inorg. Chem.* **2014**, *53*, 2708-2717.

Inorganic Chemistry
Article
pubs.acs.org/IC

Cyanomethylene-bis(phosphonate)-Based Lanthanide Complexes: Structural, Photophysical, and Magnetic Investigations**

Catalin Maxim,[†,‡] Diana G. Branzea,[†] Carmen Tiseanu,[§] Mathieu Rouzières,[⊥,¶] Rodolphe Clérac,[⊥,¶] Marius Andruh,[‡] and Narcis Avarvari*,[†]

[†]Laboratoire MOLTECH-Anjou UMR 6200, UFR Sciences, CNRS, Université d'Angers, Bât. K, 2 Bd Lavoisier, 49045 Angers, France
[‡]Faculty of Chemistry, Inorganic Chemistry Laboratory Str., University of Bucharest, Dumbrava Rosie nr. 23, 020464-Bucharest, Romania
[§]Laboratory of Solid-State Quantum Electronics, National Institute for Laser, Plasma, and Radiation Physics, P.O. Box MG-36, Magurele 077125, Romania
[⊥]CNRS, CRPP, UPR 8641, F-33600 Pessac, France
[¶]University of Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France

Supporting Information

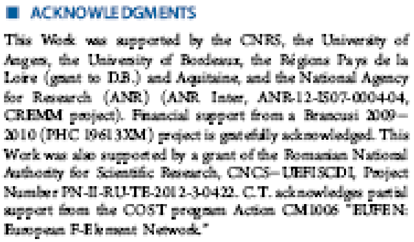
ABSTRACT: The syntheses, structural investigations, magnetic and photophysical properties of a series of 10 lanthanide mononuclear complexes, containing the heteroditopic ligand cyanomethylene-bis(5,5-dimethyl-2-oxo-1,3,2λ^5-dioxa-phosphorinane) (L), are described. The crystallographic analyses indicate two structural types: in the first one, [Ln^{III}(L)$_3$(H$_2$O)$_2$]·H$_2$O (Ln = La, Pr, Nd), the metal ions are eight-coordinated within a square antiprism geometry, while the second one, [Ln^{III}(L)$_3$(H$_2$O)]·8H$_2$O (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er), contains seven-coordinated Ln^{III} ions within distorted monocapped trigonal prisms. Intermolecular hydrogen bonding between nitrogen atoms of the cyano groups, crystallization, and coordination water molecules leads to the formation of extended supramolecular networks. Solid-state photophysical investigations demonstrate that Eu^{III} and Tb^{III} complexes possess intense luminescence with relatively long excited-state lifetimes of 530 and 1370 μs, respectively, while Pr^{III}, Dy^{III}, and Ho^{III} complexes have weak intensity luminescence characterized by short lifetimes ranging between a few nanoseconds to microseconds. The magnetic properties for Pr^{III}, Gd^{III}, Tb^{III}, Dy^{III}, and Ho^{III} complexes are in agreement with isolated Ln^{III} ions in the solid state, as suggested by the single-crystal X-ray analyses. Alternating current (ac) susceptibility measurements up to 10 kHz reveal that only the Ho^{III} complex shows a frequency-dependent ac response, with a relaxation mode clearly observed at 1.85 K around 4500 Hz.

INTRODUCTION

Functionalized acetylacetonate (acac) ligands such as 3-(4-pyridyl)-acetylacetonate (acacPy)[1] and 3-cyano-acetylacetonate (acacCN)[2] have emerged in the past decade as useful ditopical ligands combining one hard *O,O*-chelating site with one *N* donor site, which can in principle act either as ligand toward a second metal center or as hydrogen bond acceptor.

In this respect, the acacCN ligand provided monometallic Co(II),[3] Zn(II),[4] or Cu(II)[3,5] transition-metal complexes, together with heterometallic Cu(II)−Ag(I),[6] Fe(III)−Ag(I),[6] Al(III)−Ag(I),[6,7] or Cr(III)−Ag(I)[8] coordination polymers. Heteroleptic extended networks Cu(II)−Ag(I) and Co(III)−Ag(I) have also been obtained by combining acacCN and dipyrrin (dpm) ligands.[9] Interestingly, the homoleptic complexes Al(acacCN)$_3$ and Cr(acacCN)$_3$ have been investigated as sensitizers for lanthanide-centered luminescence through the preparation and photophysical properties of a series of bimetallic 2d/3d−4f complexes formulated as [(acacCN)$_2$M-(μ-acacCN)LnCl$_3$] (M = Al, Cr; Ln = Sm, Eu, Tb, Yb).[10] It is assumed in these complexes that the lanthanide ions are coordinated by one of the cyano groups of the acacCN ligands. However, the acacCN ligand is particularly well-suited to coordinate Ln centers through the *O,O*-chelating motif, as recently demonstrated by Englert et al. who described a series of Ln(acacCN)$_3$ (Ln = Ce, Eu, Yb) complexes together with their extended heterometallic Ln(acacCN)$_4$Ag networks.[11] The interest in lanthanide-based complexes resides on the one hand on their peculiar photophysical properties, as they generally have long excited-state lifetimes,[12] making them very attractive for applications such as fluorescent displays, electroluminescent devices, biomedical imaging, etc.[13] On the other hand, in the field of molecular magnetism the main recent interest is directed toward the use of highly anisotropic Ln ions, such as

Received: December 19, 2013
Published: February 20, 2014



ACKNOWLEDGMENTS

This Work was supported by the CNRS, the University of Angers, the University of Bordeaux, the Régions Pays de la Loire (grant to D.B.) and Aquitaine, and the National Agency for Research (ANR) (ANR Inter, ANR-12-IS07-0004-04, CREMM project). Financial support from a Brancusi 2009−2010 (PHC 19613XM) project is gratefully acknowledged. This Work was also supported by a grant of the Romanian National Authority for Scientific Research, CNCS−UEFISCDI, Project Number PN-II-RU-TE-2012-3-0422. C.T. acknowledges partial support from the COST program Action CM1006 "EUFEN: European F-Element Network."

Dissemination of Results 2015

3. G. Marinescu, C. Maxim, R. Clérac, M. Andruh, *$[\mathrm{Ru^{III}(valen)(CN)_2}]^-$: A New Building Block to Design 4d-4f Heterometallic Complexes*, *Inorg. Chem.* **2015**, *54*, 5621-5623.

Inorganic Chemistry
Communication
pubs.acs.org/IC

$[\mathrm{Ru^{III}(valen)(CN)_2}]^-$: a New Building Block To Design 4d−4f Heterometallic Complexes

Gabriela Marinescu,[†] Catalin Maxim,[‡] Rodolphe Clérac,*[§,∥] and Marius Andruh*[‡]

[†]"Ilie Murgulescu" Institute of Physical Chemistry, Romanian Academy, Spl. Independentei no. 202, 060021 Bucharest, Romania
[‡]Inorganic Chemistry Laboratory, Faculty of Chemistry, University of Bucharest, Str. Dumbrava Rosie no. 23, 020464 Bucharest, Romania
[§]CNRS, CRPP, UPR 8641, F-33600 Pessac, France
[∥]Univ. Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France

Supporting Information

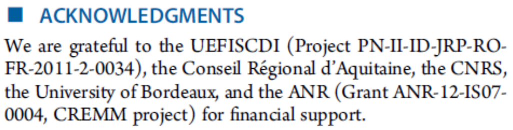
ABSTRACT: New 4d−4f heterometallic complexes with a one-dimensional structure, $^1_\infty[\{\mathrm{Ru(valen)(CN)_2KRu(valen)(CN)_2}\}\{\mathrm{Ln(O_2NO)_2(CH_3OH)_3}\}]\cdot 2\mathrm{CH_3OH}$ (Ln = Gd, Tb, Dy), have been assembled from the reaction of $[\mathrm{K(H_2O)_2Ru^{III}(valen)(CN)_2}]\cdot\mathrm{H_2O}$ with lanthanide nitrates. The exchange interaction between $\mathrm{Ru^{III}}$ and $\mathrm{Gd^{III}}$ mediated by the cyanido ligand was determined for the first time and found to be weak and of antiferromagnetic nature.

The Schiff bases derived from *o*-vanillin and various diamines are very popular ligands for obtaining binuclear 3d−4f complexes.[1] Their deprotonated forms act as side-off compartmental ligands, with each compartment interacting with a specific metal ion: the inner compartment ($\mathrm{N_2O_2}$) accommodates a 3d metal ion, while the large, outer one ($\mathrm{O_2O'_2}$) hosts more easily a lanthanide (Ln) ion. This type of binuclear complex is an excellent model platform to probe the factors governing the nature and strength of the magnetic interactions between divalent 3d metal ions and trivalent lanthanides.[2] More recently, it has been shown that the open compartment, $\mathrm{O_2O'_2}$, can also accommodate a second 3d metal ion as well.[3] In spite of the richness of the chemistry based on these ligands, binuclear complexes with a trivalent cation located within the $\mathrm{N_2O_2}$ coordination site, $[\mathrm{M^{III}Ln^{III}}]$, are unknown. A reason for that can be envisioned considering the stepwise synthesis of these heterometallic complexes. The mononuclear $\mathrm{M^{III}}$ species formed in the first step is cationic, and the interaction with the second metal cations is certainly not favored. A way to circumvent this difficulty could be to compensate for this positive charge by the addition of anionic ligands on the $\mathrm{M^{III}}$ ion within the mononuclear metalloligand. For example, these anions could coordinate to the apical positions of the $\mathrm{M^{III}}$ site. This idea is appealing, provided that the resulting anionic metalloligand is stable in solution toward dissociation of the ancillary ligands; otherwise, control over the reaction products would not be possible. In order to fulfill this condition, a metal ion that forms six very stable metal−ligand bonds must be employed. The best candidates to test this synthetic approach are thus 4d and 5d metal ions. Among these, $\mathrm{Ru^{III}}$ and $\mathrm{Os^{III}}$ ions are particularly important in molecular magnetism because they are both paramagnetic.[4] Herein we present the successful synthesis of $[\mathrm{K(H_2O)_2Ru^{III}(valen)(CN)_2}]\cdot\mathrm{H_2O}$ (**1**) as a useful precursor to design new heterometallic molecule-based magnetic materials ($\mathrm{H_2}$valen is the Schiff base resulting from the condensation reaction between *o*-vanillin and ethylenediamine). It is important to mention that the related $[\mathrm{Ru^{III}(Rsalen)(CN)_2}]^-$ complexes [$\mathrm{Rsalen^{2-}}$ stands for substituted $\mathrm{salen^{2-}}$ derivatives; $\mathrm{salen^{2-}}$ = *N,N′*-ethylenebis(salicylideneiminate)] have been used recently to construct cyanido-bridged heterometallic magnetic complexes.[5] This anionic complex $[\mathrm{Ru^{III}(valen)(CN)_2}]^-$ should be able to interact with a second metal ion through the cyanido groups or the $\mathrm{O_2O'_2}$ compartment or both of them. The coordination properties of this new metalloligand toward Ln cations ($\mathrm{Gd^{III}}$, $\mathrm{Tb^{III}}$, and $\mathrm{Dy^{III}}$) were checked, and it appears that $[\mathrm{Ru^{III}(valen)(CN)_2}]^-$ coordinates to the Ln ion only through the cyanido groups. In the final isostructural heterometallic compounds $^1_\infty[\{\mathrm{Ru(valen)(CN)_2KRu(valen)(CN)_2}\}\{\mathrm{Ln(O_2NO)_2(CH_3OH)_3}\}]\cdot 2\mathrm{CH_3OH}$ (Gd, **2**; Tb, **3**; Dy, **4**), the $\mathrm{O_2O'_2}$ coordination site stays occupied by the K ion already present in the $[\mathrm{K(H_2O)_2Ru^{III}(valen)(CN)_2}]$ precursor.

The precursor, **1**, has been obtained by adapting the synthetic protocol reported for the salen derivative (see the Supporting Information, SI).[6] Subsequently, compounds **2**−**4** have been synthesized following a similar synthetic route by heating to 50 °C for 45 min a stoichiometric mixture of **1** and $\mathrm{Ln(NO_3)_3\cdot 6H_2O}$ in methanol (see the SI). The green solution was then cooled to room temperature and filtered. Crystals suitable for X-ray crystallography were obtained by the slow diffusion of diethyl ether into the green filtrate (see the SI). The single-crystal X-ray diffraction investigation of **1** reveals the formation of a binuclear complex, with a $\mathrm{Ru^{III}}$ ion located in the $\mathrm{N_2O_2}$ coordination site (Figure 1). The two N and two O atoms from the Schiff base ligand occupy the equatorial plane of the $\mathrm{Ru^{III}}$ octahedral coordination sphere [Ru1−N1 = 1.982(9) Å; Ru1−N2 = 2.000(8) Å; Ru1−O1 = 2.018(6) Å; Ru1−O4 = 2.025(7) Å], while the cyanido ligands are positioned in apical positions [Ru−C18 = 2.064(13) Å; Ru−C19 = 2.094(13) Å]. The K ion is located in the open compartment, being coordinated by two phenoxo bridging O atoms and by two aqua ligands. Coordination of the K ion by the O atoms from the open

Received: April 18, 2015
Published: June 4, 2015

DOI: 10.1021/acs.inorgchem.5b00889
Inorg. Chem. 2015, 54, 5621−5623

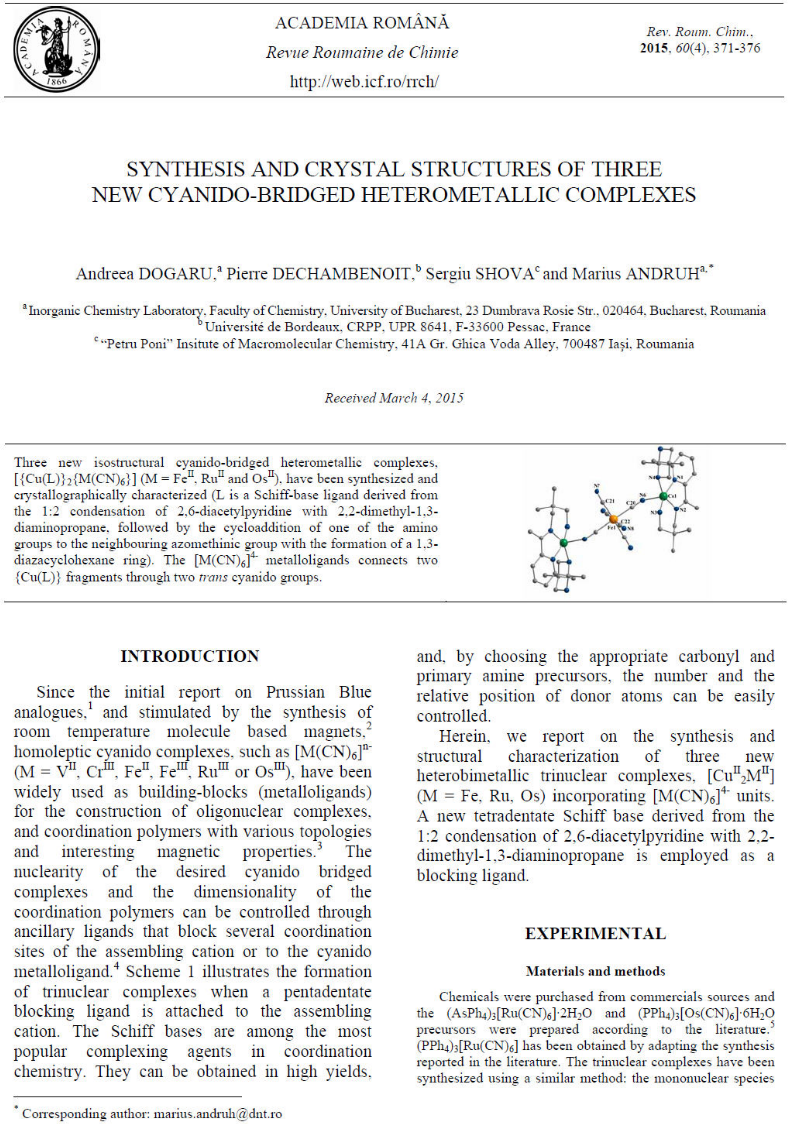


ACKNOWLEDGMENTS

We are grateful to the UEFISCDI (Project PN-II-ID-JRP-RO-FR-2011-2-0034), the Conseil Régional d'Aquitaine, the CNRS, the University of Bordeaux, and the ANR (Grant ANR-12-IS07-0004, CREMM project) for financial support.

Dissemination of Results 2015

4. A. Dogaru, C. Pichon, R. Ababei, D. Mitcov, C. Maxim, L. Toupet, C. Mathonière, R. Clérac, M. Andruh, *Synthesis and crystal structures of three new cyanido-bridged heterometallic complexes*, *Rev. Roum. Chim.* **2015**, *60(4)*, 371-376.



ACADEMIA ROMÂNĂ
Revue Roumaine de Chimie
http://web.icf.ro/rrch/

Rev. Roum. Chim.,
2015, *60*(4), 371-376

SYNTHESIS AND CRYSTAL STRUCTURES OF THREE NEW CYANIDO-BRIDGED HETEROMETALLIC COMPLEXES

Andreea DOGARU,[a] Pierre DECHAMBENOIT,[b] Sergiu SHOVA[c] and Marius ANDRUH[a,*]

[a] Inorganic Chemistry Laboratory, Faculty of Chemistry, University of Bucharest, 23 Dumbrava Rosie Str., 020464, Bucharest, Roumania
[b] Université de Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France
[c] "Petru Poni" Insitute of Macromolecular Chemistry, 41A Gr. Ghica Voda Alley, 700487 Iaşi, Roumania

Received March 4, 2015

Three new isostructural cyanido-bridged heterometallic complexes, $[\{Cu(L)\}_2\{M(CN)_6\}]$ (M = Fe^{II}, Ru^{II} and Os^{II}), have been synthesized and crystallographically characterized (L is a Schiff-base ligand derived from the 1:2 condensation of 2,6-diacetylpyridine with 2,2-dimethyl-1,3-diaminopropane, followed by the cycloaddition of one of the amino groups to the neighbouring azomethinic group with the formation of a 1,3-diazacyclohexane ring). The $[M(CN)_6]^{4-}$ metalloligands connects two {Cu(L)} fragments through two *trans* cyanido groups.

INTRODUCTION

Since the initial report on Prussian Blue analogues,[1] and stimulated by the synthesis of room temperature molecule based magnets,[2] homoleptic cyanido complexes, such as $[M(CN)_6]^{n-}$ (M = V^{II}, Cr^{III}, Fe^{II}, Fe^{III}, Ru^{III} or Os^{III}), have been widely used as building-blocks (metalloligands) for the construction of oligonuclear complexes, and coordination polymers with various topologies and interesting magnetic properties.[3] The nuclearity of the desired cyanido bridged complexes and the dimensionality of the coordination polymers can be controlled through ancillary ligands that block several coordination sites of the assembling cation or to the cyanido metalloligand.[4] Scheme 1 illustrates the formation of trinuclear complexes when a pentadentate blocking ligand is attached to the assembling cation. The Schiff bases are among the most popular complexing agents in coordination chemistry. They can be obtained in high yields, and, by choosing the appropriate carbonyl and primary amine precursors, the number and the relative position of donor atoms can be easily controlled.

Herein, we report on the synthesis and structural characterization of three new heterobimetallic trinuclear complexes, $[Cu^{II}_2M^{II}]$ (M = Fe, Ru, Os) incorporating $[M(CN)_6]^{4-}$ units. A new tetradentate Schiff base derived from the 1:2 condensation of 2,6-diacetylpyridine with 2,2-dimethyl-1,3-diaminopropane is employed as a blocking ligand.

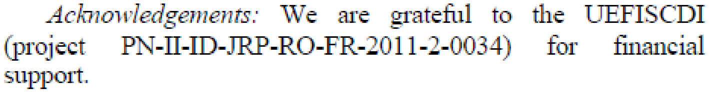
EXPERIMENTAL

Materials and methods

Chemicals were purchased from commercials sources and the $(AsPh_4)_3[Ru(CN)_6]\cdot 2H_2O$ and $(PPh_4)_3[Os(CN)_6]\cdot 6H_2O$ precursors were prepared according to the literature.[5] $(PPh_4)_3[Ru(CN)_6]$ has been obtained by adapting the synthesis reported in the literature. The trinuclear complexes have been synthesized using a similar method: the mononuclear species

---

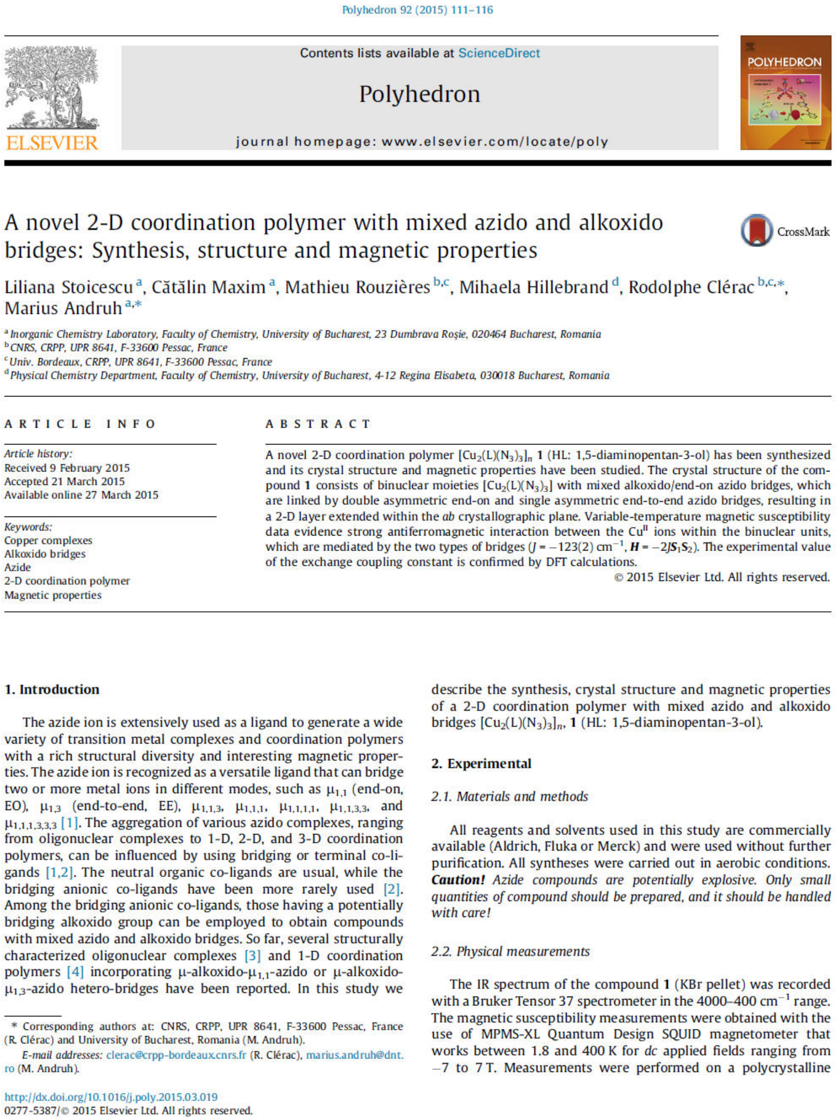
[*] Corresponding author: marius.andruh@dnt.ro



Acknowledgements: We are grateful to the UEFISCDI (project PN-II-ID-JRP-RO-FR-2011-2-0034) for financial support.

Dissemination of Results 2015

5. L. Stoicescu, C. Maxim, M. Rouzières, M. Hillebrand, R. Clérac, M. Andruh, *A novel 2-D coordination polymer with mixed azido and alkoxido bridges: Synthesis, structure and magnetic properties*, Polyhedron **2015**, *92*, 111-116.



Polyhedron 92 (2015) 111–116

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

A novel 2-D coordination polymer with mixed azido and alkoxido bridges: Synthesis, structure and magnetic properties

Liliana Stoicescu[a], Cătălin Maxim[a], Mathieu Rouzières[b,c], Mihaela Hillebrand[d], Rodolphe Clérac[b,c,*], Marius Andruh[a,*]

[a] *Inorganic Chemistry Laboratory, Faculty of Chemistry, University of Bucharest, 23 Dumbrava Roşie, 020464 Bucharest, Romania*
[b] *CNRS, CRPP, UPR 8641, F-33600 Pessac, France*
[c] *Univ. Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France*
[d] *Physical Chemistry Department, Faculty of Chemistry, University of Bucharest, 4-12 Regina Elisabeta, 030018 Bucharest, Romania*

ARTICLE INFO

Article history:
Received 9 February 2015
Accepted 21 March 2015
Available online 27 March 2015

Keywords:
Copper complexes
Alkoxido bridges
Azide
2-D coordination polymer
Magnetic properties

ABSTRACT

A novel 2-D coordination polymer $[Cu_2(L)(N_3)_3]_n$ **1** (HL: 1,5-diaminopentan-3-ol) has been synthesized and its crystal structure and magnetic properties have been studied. The crystal structure of the compound **1** consists of binuclear moieties $[Cu_2(L)(N_3)_3]$ with mixed alkoxido/end-on azido bridges, which are linked by double asymmetric end-on and single asymmetric end-to-end azido bridges, resulting in a 2-D layer extended within the *ab* crystallographic plane. Variable-temperature magnetic susceptibility data evidence strong antiferromagnetic interaction between the Cu^{II} ions within the binuclear units, which are mediated by the two types of bridges ($J = -123(2)$ cm^{-1}, $\boldsymbol{H} = -2J\boldsymbol{S}_1\boldsymbol{S}_2$). The experimental value of the exchange coupling constant is confirmed by DFT calculations.

1. Introduction

The azide ion is extensively used as a ligand to generate a wide variety of transition metal complexes and coordination polymers with a rich structural diversity and interesting magnetic properties. The azide ion is recognized as a versatile ligand that can bridge two or more metal ions in different modes, such as $\mu_{1,1}$ (end-on, EO), $\mu_{1,3}$ (end-to-end, EE), $\mu_{1,1,3}$, $\mu_{1,1,1}$, $\mu_{1,1,1,1}$, $\mu_{1,1,3,3}$, and $\mu_{1,1,1,3,3,3}$ [1]. The aggregation of various azido complexes, ranging from oligonuclear complexes to 1-D, 2-D, and 3-D coordination polymers, can be influenced by using bridging or terminal co-ligands [1,2]. The neutral organic co-ligands are usual, while the bridging anionic co-ligands have been more rarely used [2]. Among the bridging anionic co-ligands, those having a potentially bridging alkoxido group can be employed to obtain compounds with mixed azido and alkoxido bridges. So far, several structurally characterized oligonuclear complexes [3] and 1-D coordination polymers [4] incorporating μ-alkoxido-$\mu_{1,1}$-azido or μ-alkoxido-$\mu_{1,3}$-azido hetero-bridges have been reported. In this study we describe the synthesis, crystal structure and magnetic properties of a 2-D coordination polymer with mixed azido and alkoxido bridges $[Cu_2(L)(N_3)_3]_n$, **1** (HL: 1,5-diaminopentan-3-ol).

2. Experimental

2.1. Materials and methods

All reagents and solvents used in this study are commercially available (Aldrich, Fluka or Merck) and were used without further purification. All syntheses were carried out in aerobic conditions. ***Caution!*** *Azide compounds are potentially explosive. Only small quantities of compound should be prepared, and it should be handled with care!*

2.2. Physical measurements

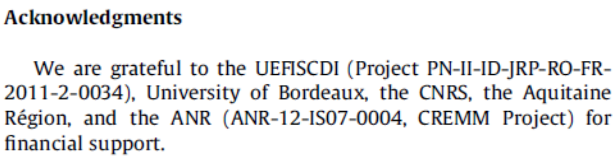
The IR spectrum of the compound **1** (KBr pellet) was recorded with a Bruker Tensor 37 spectrometer in the 4000–400 cm^{-1} range. The magnetic susceptibility measurements were obtained with the use of MPMS-XL Quantum Design SQUID magnetometer that works between 1.8 and 400 K for *dc* applied fields ranging from −7 to 7 T. Measurements were performed on a polycrystalline

---

[*] Corresponding authors at: CNRS, CRPP, UPR 8641, F-33600 Pessac, France (R. Clérac) and University of Bucharest, Romania (M. Andruh).

E-mail addresses: clerac@crpp-bordeaux.cnrs.fr (R. Clérac), marius.andruh@dnt.ro (M. Andruh).

http://dx.doi.org/10.1016/j.poly.2015.03.019

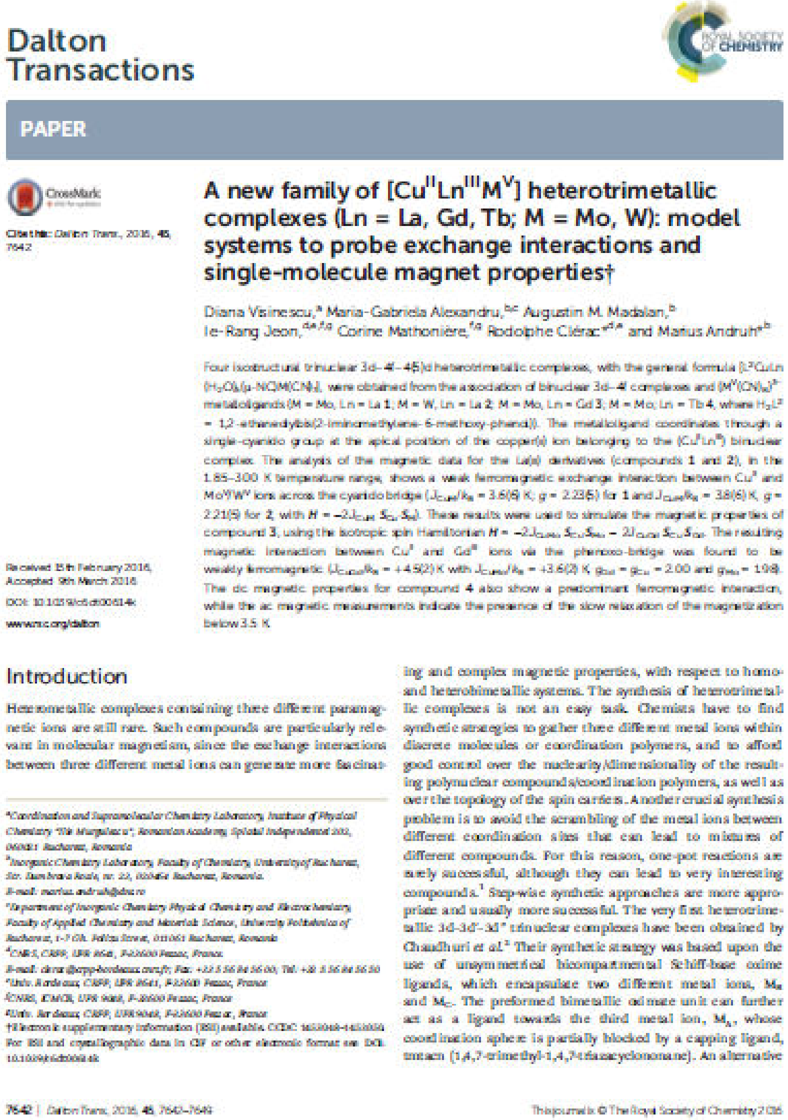


Acknowledgments

We are grateful to the UEFISCDI (Project PN-II-ID-JRP-RO-FR-2011-2-0034), University of Bordeaux, the CNRS, the Aquitaine Région, and the ANR (ANR-12-IS07-0004, CREMM Project) for financial support.

Dissemination of Results 2016

6. D. Visinescu, M.-G. Alexandru, A. M. Madalan, I.-R. Jeon, C. Mathonière, R. Clérac, M. Andruh, *A new family of [Cu^{II}Ln^{III}M^{V}] heterotrimetallic complexes (Ln = La, Gd, Tb; M = Mo, W): Model systems to probe exchange interactions and Single-Molecule Magnet properties*, *Dalton Trans.* **2016**, *45*, 7642-7649.



Dalton Transactions

PAPER

Cite this: Dalton Trans., 2016, 45, 7642

A new family of [Cu^{II}Ln^{III}M^{V}] heterotrimetallic complexes (Ln = La, Gd, Tb; M = Mo, W): model systems to probe exchange interactions and single-molecule magnet properties†

Diana Visinescu,[a] Maria-Gabriela Alexandru,[b,c] Augustin M. Madalan,[b]
Ie-Rang Jeon,[d,e,f,g] Corine Mathonière,[f,g] Rodolphe Clérac*[d,e] and Marius Andruh*[b]

Four isostructural trinuclear 3d–4f–4(5)d heterotrimetallic complexes, with the general formula [L^{2}CuLn(H$_2$O)$_4$(μ-NC)M(CN)$_7$], were obtained from the association of binuclear 3d–4f complexes and [M^V(CN)$_8$]$^{3-}$ metalloligands (M = Mo, Ln = La **1**; M = W, Ln = La **2**; M = Mo, Ln = Gd **3**; M = Mo, Ln = Tb **4**, where H$_2$L^2 = 1,2-ethanediylbis(2-iminomethylene-6-methoxy-phenol)). The metalloligand coordinates through a single-cyanido group at the apical position of the copper(II) ion belonging to the {Cu^{II}Ln^{III}} binuclear complex. The analysis of the magnetic data for the La(III) derivatives (compounds **1** and **2**), in the 1.85–300 K temperature range, shows a weak ferromagnetic exchange interaction between Cu^{II} and Mo^V/W^V ions across the cyanido bridge (J_{CuMo}/k_B = 3.6(6) K, g = 2.23(5) for **1** and J_{CuW}/k_B = 3.8(6) K, g = 2.21(5) for **2**, with $H = -2J_{CuM}\,S_{Cu}\,S_M$). These results were used to simulate the magnetic properties of compound **3**, using the isotropic spin Hamiltonian $H = -2J_{CuMo}\,S_{Cu}S_{Mo} - 2J_{CuGd}\,S_{Cu}S_{Gd}$. The resulting magnetic interaction between Cu^{II} and Gd^{III} ions via the phenoxo-bridge was found to be weakly ferromagnetic (J_{CuGd}/k_B = +4.5(2) K with J_{CuMo}/k_B = +3.6(2) K, g_{Gd} = g_{Cu} = 2.00 and g_{Mo} = 1.98). The dc magnetic properties for compound **4** also show a predominant ferromagnetic interaction, while the ac magnetic measurements indicate the presence of the slow relaxation of the magnetization below 3.5 K.

Received 15th February 2016,
Accepted 9th March 2016

DOI: 10.1039/c6dt00614k

www.rsc.org/dalton

Introduction

Heterometallic complexes containing three different paramagnetic ions are still rare. Such compounds are particularly relevant in molecular magnetism, since the exchange interactions between three different metal ions can generate more fascinating and complex magnetic properties, with respect to homo- and heterobimetallic systems. The synthesis of heterotrimetallic complexes is not an easy task. Chemists have to find synthetic strategies to gather three different metal ions within discrete molecules or coordination polymers, and to afford good control over the nuclearity/dimensionality of the resulting polynuclear compounds/coordination polymers, as well as over the topology of the spin carriers. Another crucial synthesis problem is to avoid the scrambling of the metal ions between different coordination sites that can lead to mixtures of different compounds. For this reason, one-pot reactions are rarely successful, although they can lead to very interesting compounds.[1] Step-wise synthetic approaches are more appropriate and usually more successful. The very first heterotrimetallic 3d–3d′–3d″ trinuclear complexes have been obtained by Chaudhuri *et al.*[2] Their synthetic strategy was based upon the use of unsymmetrical bicompartmental Schiff-base oxime ligands, which encapsulate two different metal ions, M$_B$ and M$_C$. The preformed bimetallic oximate unit can further act as a ligand towards the third metal ion, M$_A$, whose coordination sphere is partially blocked by a capping ligand, tmtacn (1,4,7-trimethyl-1,4,7-triazacyclononane). An alternative

---

[a] *Coordination and Supramolecular Chemistry Laboratory, Institute of Physical Chemistry "Ilie Murgulescu", Romanian Academy, Splaiul Independentei 202, 060021 Bucharest, Romania*

[b] *Inorganic Chemistry Laboratory, Faculty of Chemistry, University of Bucharest, Str. Dumbrava Rosie, nr. 23, 020464 Bucharest, Romania. E-mail: marius.andruh@dnt.ro*

[c] *Department of Inorganic Chemistry, Physical Chemistry and Electrochemistry, Faculty of Applied Chemistry and Materials Science, University Politehnica of Bucharest, 1-7 Gh. Polizu Street, 011061 Bucharest, Romania*

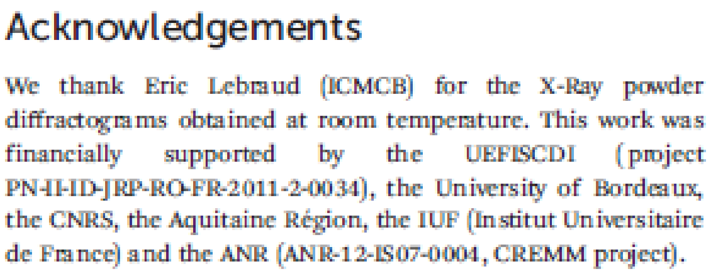
[d] *CNRS, CRPP, UPR 8641, F-33600 Pessac, France. E-mail: clerac@crpp-bordeaux.cnrs.fr; Fax: +33 5 56 84 56 00; Tel: +33 5 56 84 56 50*

[e] *Univ. Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France*

[f] *CNRS, ICMCB, UPR 9048, F-33600 Pessac, France*

[g] *Univ. Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France*

† Electronic supplementary information (ESI) available. CCDC [illegible]. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt00614k



Acknowledgements

We thank Eric Lebraud (ICMCB) for the X-Ray powder diffractograms obtained at room temperature. This work was financially supported by the UEFISCDI (project PN-II-ID-JRP-RO-FR-2011-2-0034), the University of Bordeaux, the CNRS, the Aquitaine Région, the IUF (Institut Universitaire de France) and the ANR (ANR-12-IS07-0004, CREMM project).

Dissemination of Results 2016

CONFERENCES

1. **M. Andruh**, “*Heterostrispin complexes*”, The VIIth International conference «High-Spin Molecules and Molecular Magnets», Novosibirsk, Russia, September 19-23, 2016 - prezentare orală - keynote speaker;

2. **M. Andruh**, “*Chiral Schiff bases in designing magnetic complexes and catalysts*”, The 42nd International Conference on Coordination Chemistry, Brest, France, July 3-8, 2016, prezentare orală - invited speaker;

3. **M. Andruh**, “*Chiral Schiff bases in designing magnetic complexes and catalysts*”, The 8th International Conference on Materials Science and Condensed Matter Physics, Chisinau, Moldova, September 12-16, 2016, prezentare orală - plenary lecture;

4. **A.A. Patrascu**, S. Calancea, R.A. Allão Cassaro, S. Soriano, A. M. Madalan, C. Maxim, M. A. Novak, N. Avarvari, M. G. F. Vaz, M. Andruh, “*Heterospin 3d-4f and 2p-3d-4f complexes. Synthesis, crystal structures and magnetic properties*”, The 42nd International Conference on Coordination Chemistry, Brest, France, July 3-8, 2016, poster.

Dissemination of Results **2016**

WORKSHOP

“Crystal Engineering of Multifunctional Molecule-Based Materials”

2nd-6th May 2016, Sinaia, Romania

- 30 de participanţi;
- din partea franceză, partenerii de proiect: Dr. Marc Fourmigué, Dr. Narcis Avarvari, Dr. Rodolphe Clérac;
- invitaţi: Prof. Dominique Luneau (Lyon); Dr. Jean-Pascal Sutter (Toulouse), Prof. Manuel Almeida (Lisabona);
- conferinţa finală a fost prezentată de către **Prof. Jean-Marie Lehn**, laureat al Premiului Nobel pentru Chimie.
- o atenţie specială a fost acordată membrilor tineri din echipa, care au făcut prezentări orale.

PROGRAM WORKSHOP

Tuesday, May 2		
9.00 – 9.30	Opening	
9.30 – 10.10	Rodolphe Clérac	*Optical and Magnetic Molecular Switches Based on Metal-to-Metal Electron Transfer Mechanism:*
10.10 – 10.30	Diana Visinescu	*3d-4f-4(5)d heterotrimetallic nanomagnets*
10.30 – 11.10	Nicolas Mercier	*Aggregation Induced Phosphorescence and Mechanochromic Luminescence Properties of Bi(III) or Pb(II) Bipyridine-N-oxide based Compounds*
11.10 – 11.30	Coffee break	
11.30 – 12.10	Narcis Avarvari	*Chiral methylated BEDT-TTF, EDT-TTF and metal-dithiolene derivatives*
12.10 – 12.30	Maria Alexandru	*Cyanido metalloligands. Toward heterometallic complexes.*
12.30 – 13.10	Dominique Luneau	*Coordination chemistry of nitronyl nitroxide radicals. A radical tool for molecule based multifunctional materials*
13.10 – 14.30	Lunch	
14.30 – 15.10	Manuel Almeida	*Magnetism and SMM behavior in Layered lanthanide and Uranium compounds*
15.10 – 15.30	Andreea Dogaru	*Cyanido-bridged heterometallic systems*
15.30 – 16.10	Karine Heuzé	*Functionalization of Core-Shell Magnetic Nanoparticles for Bio-Immobilization and Catalysis*
16.10 – 16.50	Abdelkrim El-Ghayoury	*Metal Induced Modulation of Electronic & Optical Properties of Multifunctional Ligands*
Wednesday, May 3		
9.00 – 9.40	Marc Fourmigué	*Halogen bonding in conducting and magnetic solids*
9.40 – 10.00	Mihaela Mocanu	*New oligonuclear complexes derived from $M^{II}(hfac)_2$ precursors. Synthesis and characterization.*
10.00 – 10.40	Jean-Pascal Sutter	*H-Bond Stitched Nano-Porous Molecular Framework Materials*
10.40 -	Coffee break, social program (Peles Castle), lunch	
17.00 – 19.00	Meeting ANR – Rapport final	
Thursday, May 4		
11.00 – 12.00	**Jean-Marie Lehn**	***Dynamic Materials. Towards Functional Adaptive Materials.***
12.00 – 12.20	Cristian Ene	*Mononuclear lanthanide(III) complexes of symmetrical tripodal ligands - structural investigations to elucidate biochemical interactions*
12.20 – 12.40	Catalin Maxim	*Multimetallic complexes obtained by single-crystal-to-single-crystal transformations*
12.40 – 13.00	Teodora Mocanu	*Organometallic and tetrahedral spacers - new tectons in crystal engineering and metallosupramolecular chemistry*
13:00 – 14:30	Lunch	
14.30 – 14:50	Daniel Rosario-Amorin	*Soft materials based on molecular magnets and spin switches*
14:50 – 15:20	Catalin Anghel	*2,5-Disubstituted-1,3,4-oxadiazols based ligands*
15:20 – 15:40	Adrian Apostol	*Homo and heterometallic oligonuclear complexes of Co(II), Co(III) and Ni(II) containing aminoalchools and carboxilate anions*
16:00	Closing	