Universitatea din Bucuresti

**Universitatea Babes-Bolyai
Cluj-Napoca**

DESIGN OF ORGANIC SPACERS FOR CONSTRUCTING METAL- ORGANIC FRAMEWORKS (MOFs) – TOWARDS A BETTER CONTROL OF THE POROUS ARCHITECTURE AND ACTIVE CATALYTIC SITES

Financial support: UEFISCDI

INOVARE SI CREATIVITATE

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

Project Code: PN-II-ID-PCCE-2011-2-0050 (9/2012)

Project timespan: 2012 – 2016

Partners and Management

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Team 2 – University of Bucharest, Faculty of Chemistry

Team 2 leader: Prof. Dr. Vasile Parvulescu

Team 3 – Babes-Bolyai University, Faculty of Chemistry & Chemical Engineering

Team 3 leader: Prof. Dr. Ion Grosu

Team 4 – Babes-Bolyai University, Faculty of Chemistry & Chemical Engineering

Team 4 leader: Prof. Dr. Cristian Silvestru

Project Teams

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Dr. Adrian Ion
Dr. Traian Pasatoiu
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Drd. Alina Dinca
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Dr. Anamaria Terec
Dr. Ioana Georgeta Grosu
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Tehn. Szablocs Szima
Tehn. Maria Pascanu
Tehn. Mihai Levi Gabrian

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Dr. Ciprian I. Rat
Dr. Albert Soran
Dr. Alexandra Pop
Dr. Alpar Pollnitz
Ac. Florin Adascalitei
Drd. Gabriela Strîmb
Drd. Marian Olaru
Tehn. Răzvan Şuteu
Tehn. Atena Solea
Tehn. Ileana Oprea
Tehn. Adrian Somesan
Tehn. Roxana Popa

Project Budget

No.	BUDGET CHAPTER (EXPENSES)	2012 (lei)	2013 (lei)	2014 (lei)	2015 (lei)	2016 (lei)	TOTAL (lei)
1	**SALARIES**	388 732,35	814 511,19	795 309,89	394 998,14	202 995,86	2 596 547,43
2	**OVERHEAD**	205 220,72	106 177,27	151 832,82	123 861,53	91 657,66	678 750
3	**MOBILITY**	1 563,23	30 055,22	31 859,58	39 478,49	73 934,51	176 891,03
4	**INVENTORY**	1 434 483,7	338 631,32	312 997,71	858 271,84	603 426,97	3 547 811,54
	TOTAL BUDGET	**2 030 000**	**1 289 375**	**1 292 000**	**1 416 610**	**972 015**	**7 000 000**

Summary

The project proposes a systematic study of a novel generation of metal-organic frameworks (MOFs) based on made-by-design organo-metallic tectons.

A special emphasis will be given to the post-synthesis processing of the new MOFs: removal of solvent and weakly coordinated ligands; functionalization by nanoconfinement with metal nanoparticles and generation of acidic and basic sites.

The properties of the newly synthesized MOFs will be investigated as follows:

- sorption capacity of various gases (H_2, CO_2, C_2H_2, etc.)
- catalytic properties (e.g. enantioselective organic reactions catalyzed by chiral MOFs or asymmetric aldol reactions between representative ketones and aromatic aldehydes, under solvent-free conditions, using functionalized MOFs with acidic and basic sites)
- luminescent properties and the influence brought by host molecules
- ability to play a role in decontamination processes (e.g. as adsorbents for the molecules resulted from degradation of pharmaceutical compounds via either liquid phase catalytic oxidation or plasma)

Objectives

Main objectives:

A. Design, synthesis and characterization of new families of organic spacers

B. Design, synthesis and characterization of new organometallic spacers and potential organometallic nodes.

C. Building MOFs based on the newly designed and synthesized organic and organometallic spacers.

D. Optimization of MOFs architectures based on the design improvement of new spacers and organometallic nodes.

E. Optimizing MOFs properties by post-synthesic processes.

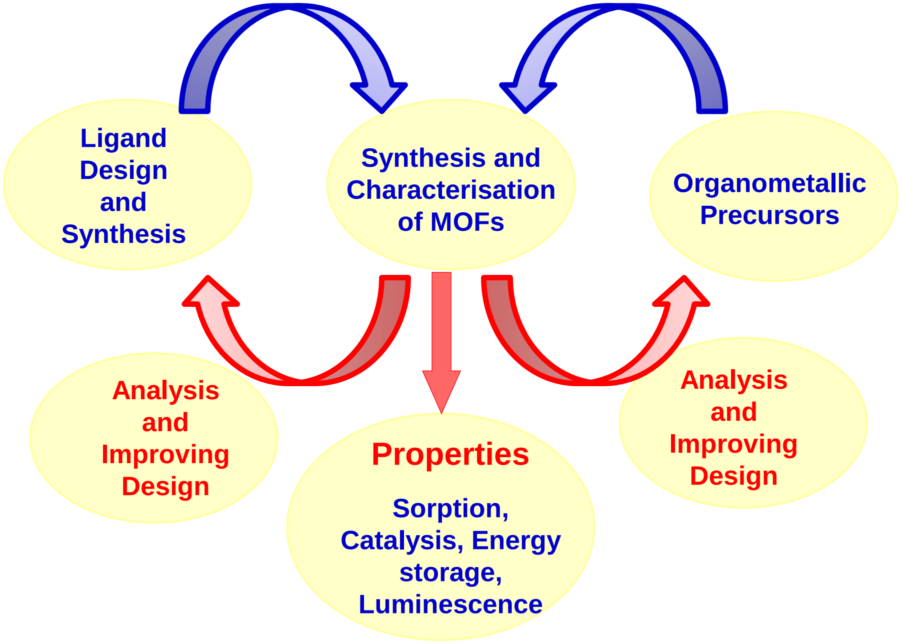
F. Generation of acidic and basic sites in MOFs showing optimized properties by nanoconfinement with metal nanoparticles and post-synthetic functionalization.

G. Evaluation of selective sorption capacity of MOFs for various molecules.

H. Investigation of gas (hydrogen) storage capability of synthesized MOFs for energy applications.

Project Organization

The goal of the project is to provide a rational design for the synthesis of new MOFs and to prove their effectiveness in several applications, such as catalysis, energy storage, luminescence, etc.



Ligand Design and Synthesis

Synthesis and Characterisation of MOFs

Organometallic Precursors

Analysis and Improving Design

Properties

Sorption, Catalysis, Energy storage, Luminescence

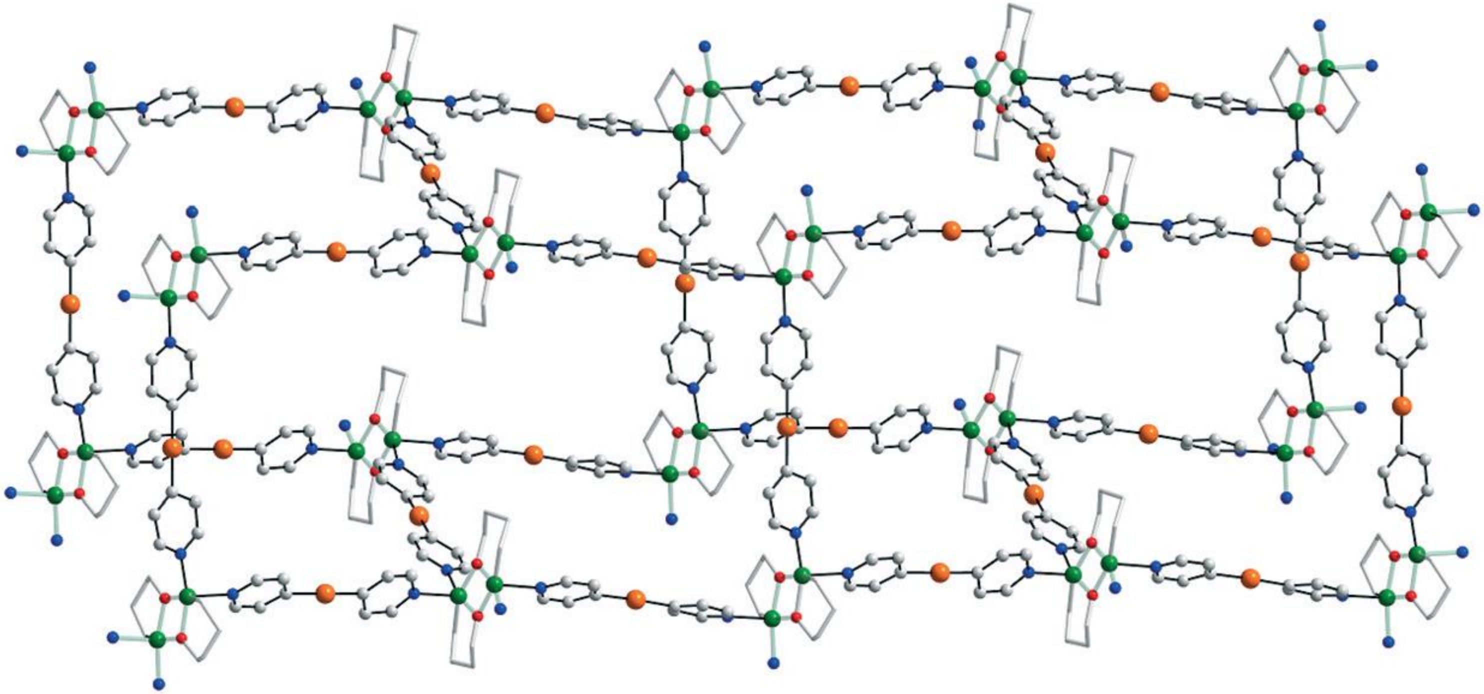
Analysis and Improving Design

Milestones

- organic and organometallic tectons; new families of MOFs based on layered cyclophanes, C_3 cryptocyclophanes and new tetrahedral spacers
- MOFs with high capability for the storage of gases and/or high catalytical activity
- luminescent and/or chiral materials

Major Scientific Results

- ❑ **Design of novel coordination polymers using organometallic spacers and nodes**

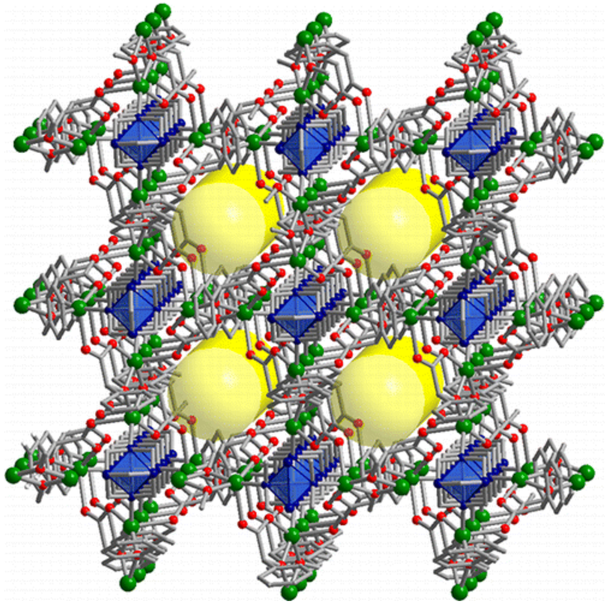


The first 3-D coordination polymer constructed from binuclear alkoxo-bridged nodes and linear spacers – $[Cu(pa)_2(py_2Hg)_2] (BF_4)_2$

T. Mocanu, C.I. Rat, C. Maxim, S. Shova, V. Tudor, C. Silvestru, M. Andruh, *Bis(4-pyridyl)mercury – a new linear tecton in crystal engineering: coordination polymers and co-crystallization processes*, *CrystEngComm*, **2015**, *17*, 5474-5487.

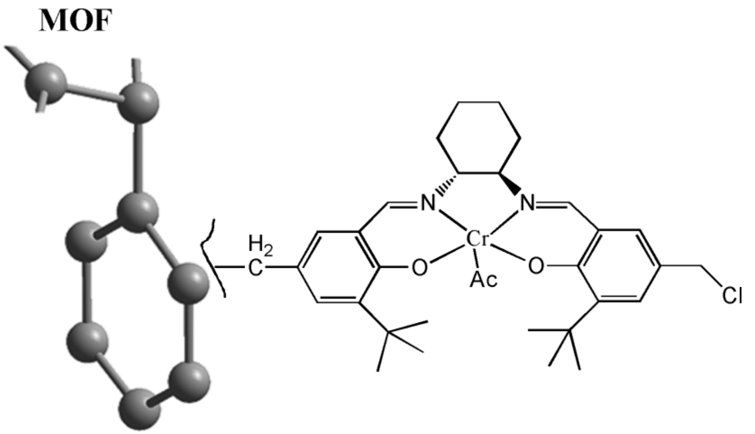
Major Scientific Results

- **Design of 3-D coordination networks for gas sorption and postsynthetic modifications for catalysis**



3-D metal−organic framework, ${}^{3}_{\infty}[Cu_2(mand)_2(hmt)]\cdot H_2O$

Ilyes, E.; Florea, M.; Madalan, A.M.; Haiduc, I.; Parvulescu, V.I.; Andruh, M., *A Robust Metal-Organic Framework Constructed from Alkoxo-Bridged Binuclear Nodes and Hexamethylenetetramine Spacers: Crystal Structure and Sorption Studies*, *Inorg. Chem.* **2012**, *51*, 7954-7956.

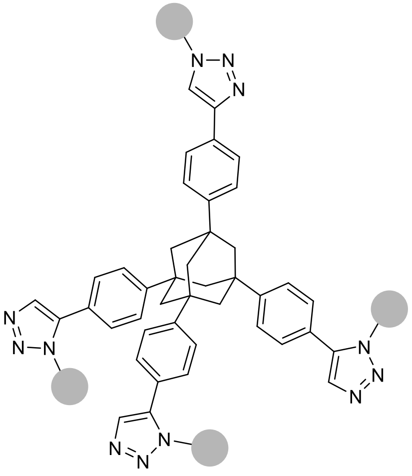


Grafting of the chiral, dimeric Cr^{III}–salen complex onto $[Cu_2(mand)_2(hmt)]$

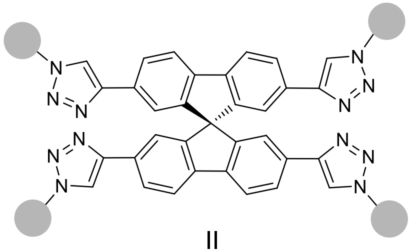
Candu, N.; Tudorache, M.; Florea, M.; Ilyes, E.; Vasiliu, F.; Mercioniu, I.; Coman, S.M.; Haiduc, I.; Andruh, M.; Parvulescu, V.I., *Postsynthetic modification of a Metal-Organic Framework (MOF) Structure for Enantioselective Catalytic Epoxidation*, *ChemPlusChem* **2013**, *78*, 443-450.

Major Scientific Results

- **Synthesis of new organic ligands with tetrahedral symmetry**



I



II

● = nucleobases (uracil, thymine, adenine) decorated groups

New rigid nucleobase-decorated tetrapodants exhibiting 1,3,5,7-tetraphenyladamantane and 9,9'-spirobifluorene central units

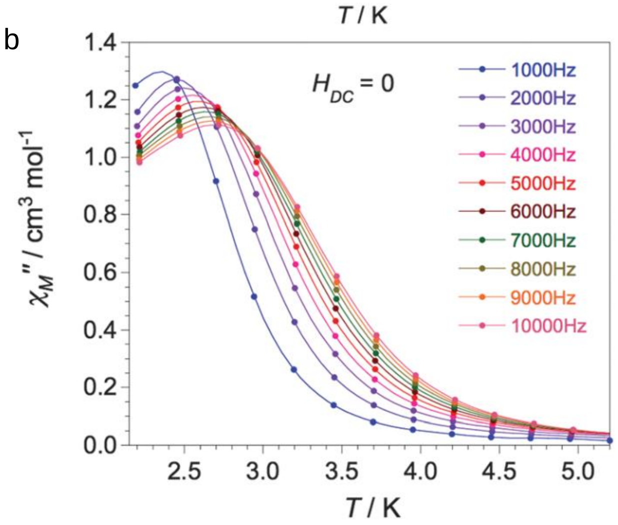
- **Synthesis of new polycarboxylates spacers for constructing coordination polymers**

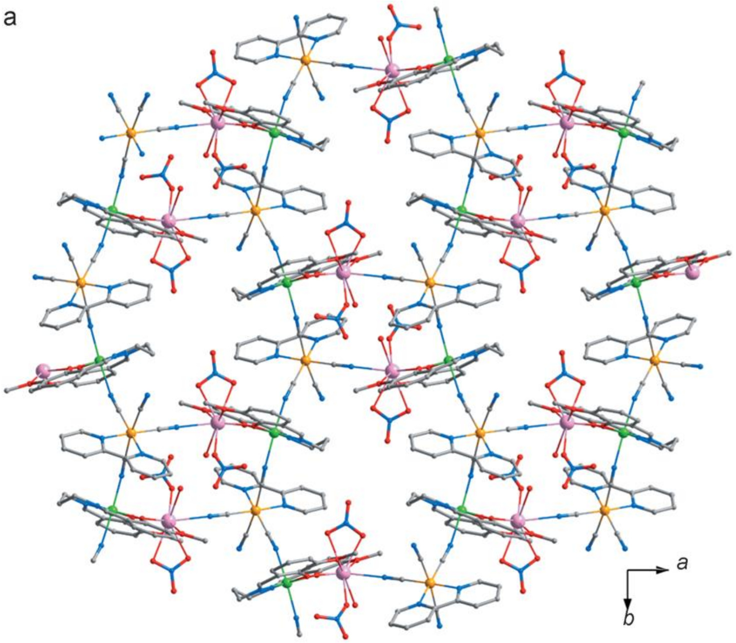
L. Pop, M.L. Golban, N.D. Hadade, C. Socaci, I. Grosu, *CuAAC Synthesis of Tetragonal Building Blocks Decorated with Nucleobases*, *SYNTHESIS-STUTTGART*, **2015**, *47*, 2799-2802.

Major Scientific Results

❑ **Investigation of enantioselective organic reactions catalyzed by chiral MOFs**

❑ **Design of heterotrimetallic coordination polymers displaying slow relaxation of the magnetization**



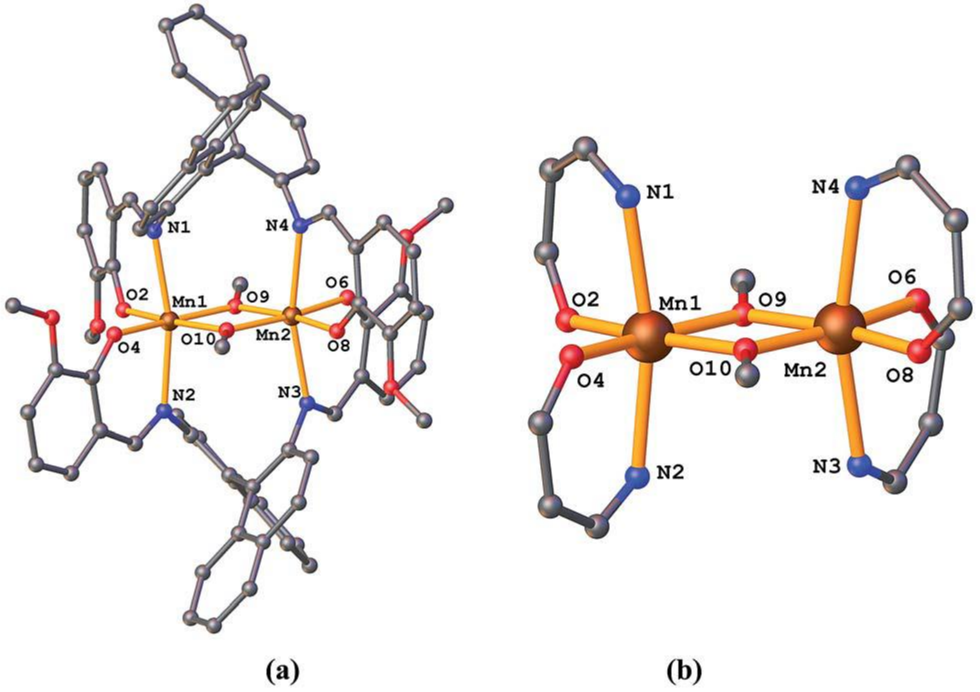


a. 2-D coordination network of $\{Ni^{II}Tb^{III}Fe^{III}\}$
b. The heterotrimetallic compound exhibits slow relaxation of the magnetization

M.G. Alexandru, D. Visinescu, M. Andruh, N. Marino, D. Armentano, J. Cano, F. Lloret, M. Julve, *Heterotrimetallic coordination polymers: $\{Cu^{II}Ln^{III}Fe^{III}\}$ chains and $\{Ni^{II}Ln^{III}Fe^{III}\}$ layers: Synthesis, crystal structures, and magnetic properties*, Chemistry A European Journal, **2015**, *21*, 5429-5446.

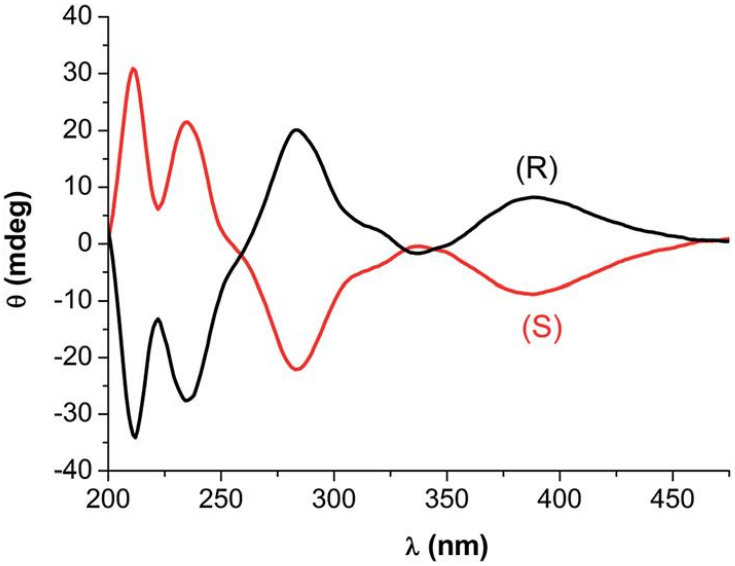
Major Scientific Results

❑ Design of novel coordination polymers using chiral nodes



(a) Perspective view of the $[Mn^{III}_2(\mu\text{-}OCH_3)_2(S\text{-}valBINAM)_2]\cdot 2DMF$ enantiomer.
(b) Detail showing the two homochiral chromophores.

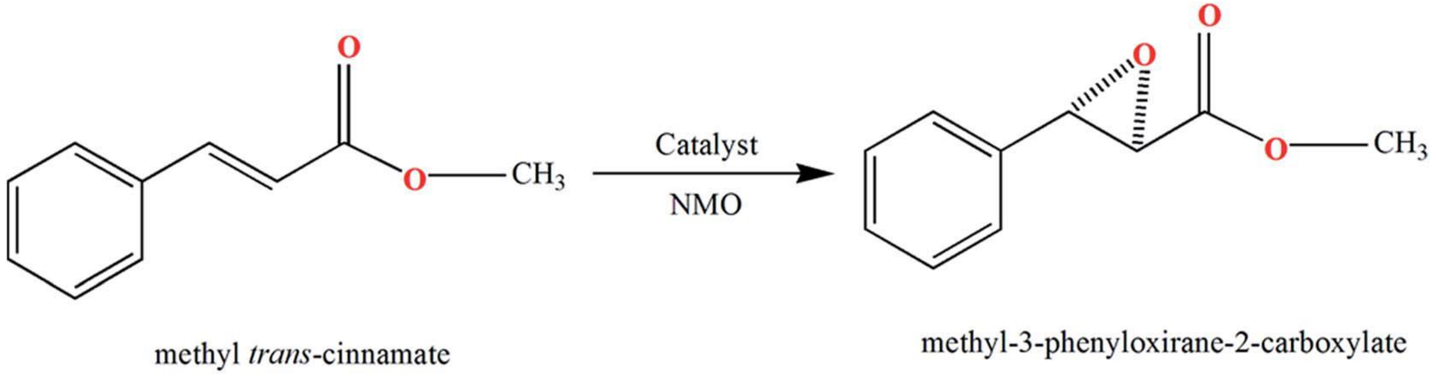
CD spectra for the two enantiomers, $[Mn^{III}_2(\mu\text{-}OCH_3)_2(R\text{-}valBINAM)_2]$ and $[Mn^{III}_2(\mu\ \text{-}OCH_3)_2(S\text{-}valBINAM)_2]$.



A. S. Dinca, N. Candu, S. Shova, F. Lloret, M. Julve, V. I. Parvulescu, M. Andruh, *A new chiral dimanganese(III) complex: synthesis, crystal structure, spectroscopic, magnetic, and catalytic properties*, *RSC Adv*., **2016,** *6*, 86569

Major Scientific Results

❑ Catalytic properties of novel coordination polymers using chiral nodes



methyl *trans*-cinnamate

methyl-3-phenyloxirane-2-carboxylate

Methyl trans-cinnamate epoxidation catalyzed by the complexes 1 and 2.

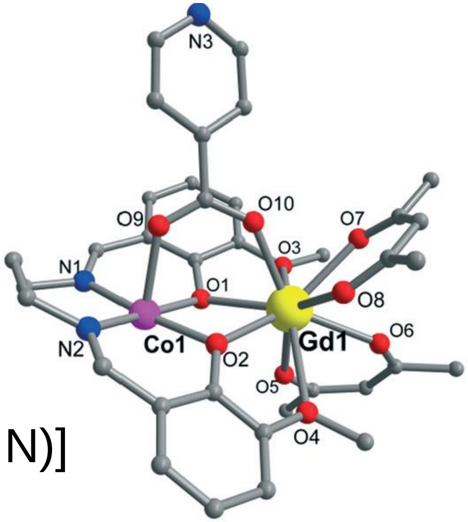
Reactie	Catalizator	Selectivitate in epoxid (%)	TOF (h^{-1})	
			EtOH (solvent)	IPA (solvent)
1	Faracatalizator	-	-	-
2	$[Mn^{III}_2(CH_3O)_2(S\text{-valBINAM})_2]$	>99.9 (*S*)	0.03	-
3	$[Mn^{III}_2(CH_3O)_2(S\text{-valBINAM})_2]$	>99.9 (*S*)	-	$4.8 \cdot 10^{-3}$
4	$[Mn^{III}_2(CH_3O)_2(R\text{-valBINAM})_2]\cdot$	>99.9 (*R*)	0.04	-
5	$[Mn^{III}_2(CH_3O)_2(R\text{-valBINAM})_2]\cdot$	>99.9 (*R*)	-	$7.3 \cdot 10^{-3}$

Reaction conditions: 0.162 g TMC (1 mmol), 8.1 mg of catalyst, Et3N = 0.1 g, (N-methylmorpholine-N-oxide) = 0.1757 g, 72 h, 6 mL EtOH : H2O (5 : 1 v/v) or IPA : H_2O (5 : 1 v/v) solvent mixtures.

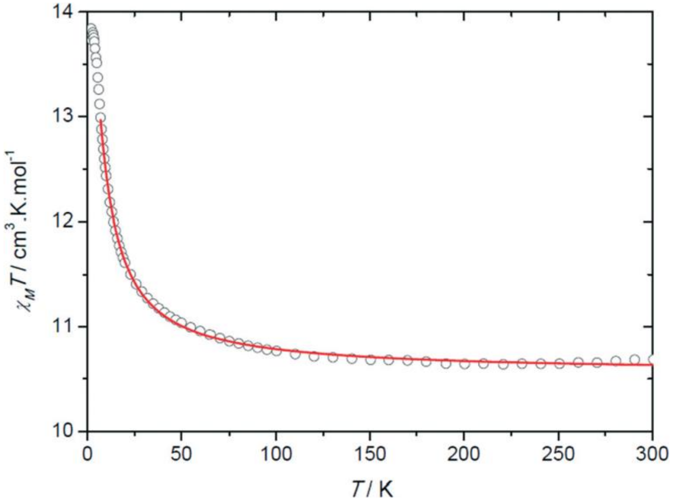
A. S. Dinca, N. Candu, S. Shova, F. Lloret, M. Julve, V. I. Parvulescu, M. Andruh, *A new chiral dimanganese(III) complex: synthesis, crystal structure, spectroscopic, magnetic, and catalytic properties, RSC Adv*., **2016,** *6*, 86569

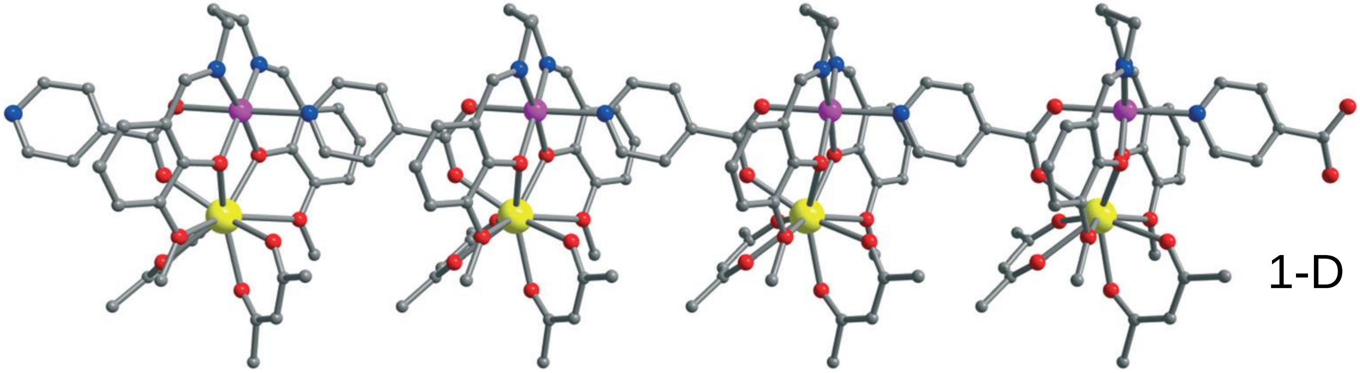
Major Scientific Results

❑ One-dimensional coordination polymers constructed from binuclear 3d–4f nodes and isonicotinato spacer



Asymmetric unit
$[Co(valpn)Gd(hfac)_2(IN)]$



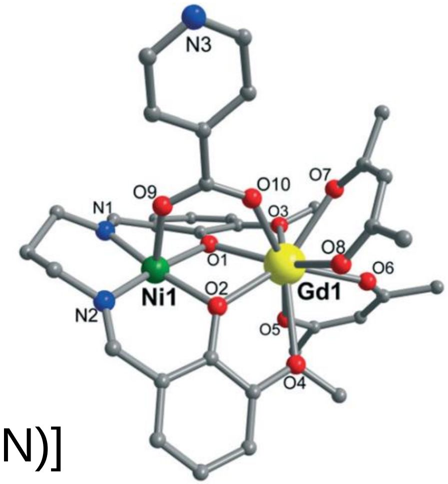


1-D coordination polymer

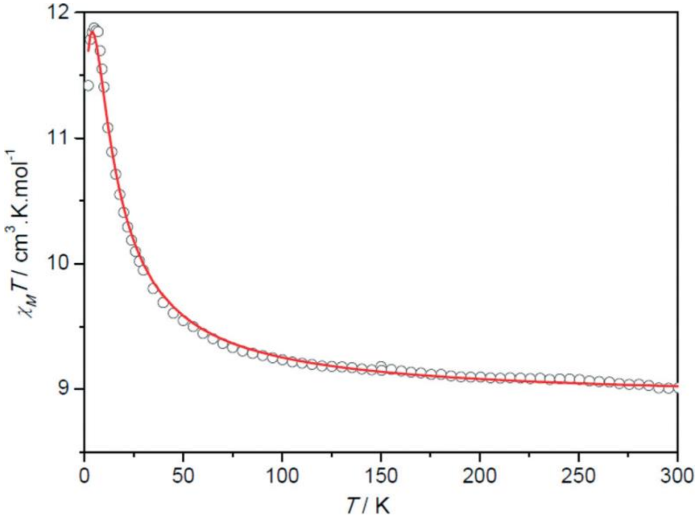
A. A. Patrascu, S. Calancea, R. A. Allão Cassaro,S Soriano, A. M. Madalan, C. Maxim,M. A. Novak, M. G. F. Vaz, M. Andruh, *One-dimensional coordination polymers, constructed from binuclear 3d-4f nodes and isonicotinato spacers*, *CrystEngComm.*, **2016**, *18*, 4779.

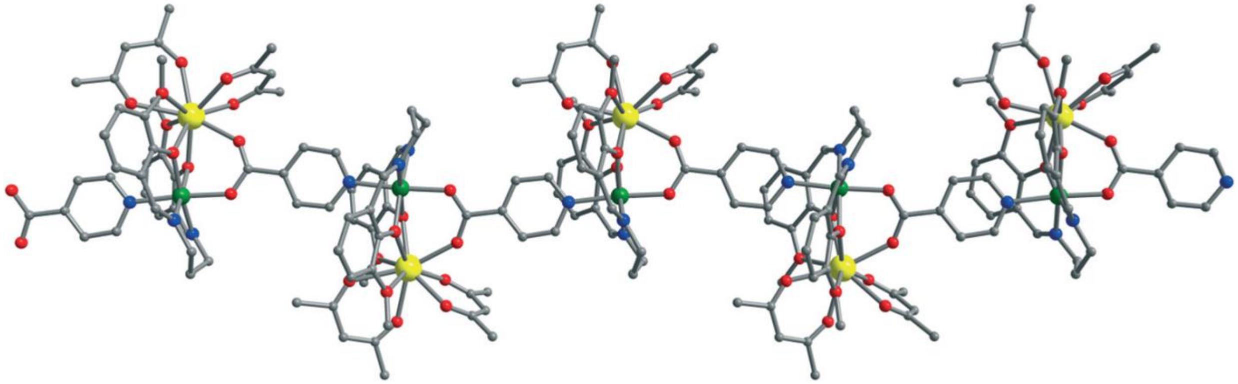
Major Scientific Results

- **One-dimensional coordination polymers constructed from binuclear 3d–4f nodes and isonicotinato spacer**



Asymmetric unit
[Ni(valpn)Gd(hfac)$_2$(IN)]



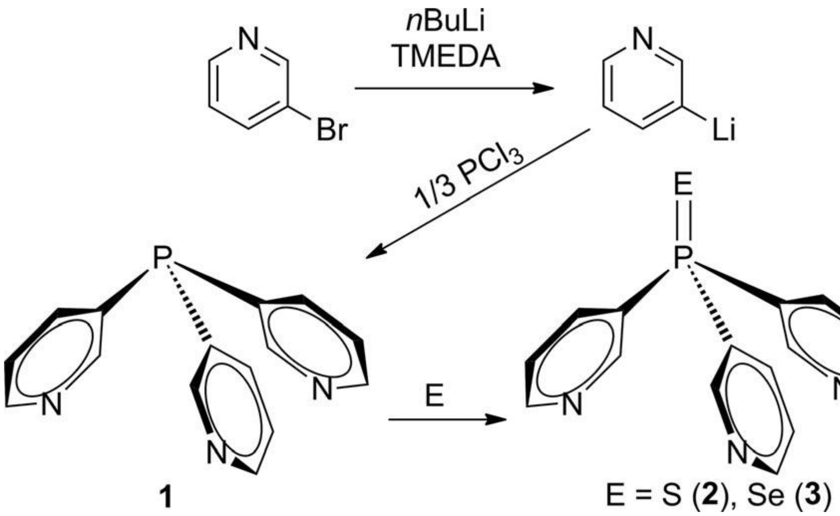


1-D coordination polymer

A. A. Patrascu, S. Calancea, R. A. Allão Cassaro,S Soriano, A. M. Madalan, C. Maxim,M. A. Novak, M. G. F. Vaz, M. Andruh, *One-dimensional coordination polymers, constructed from binuclear 3d-4f nodes and isonicotinato spacers*, *CrystEngComm.*, **2016**, *18*, 4779.

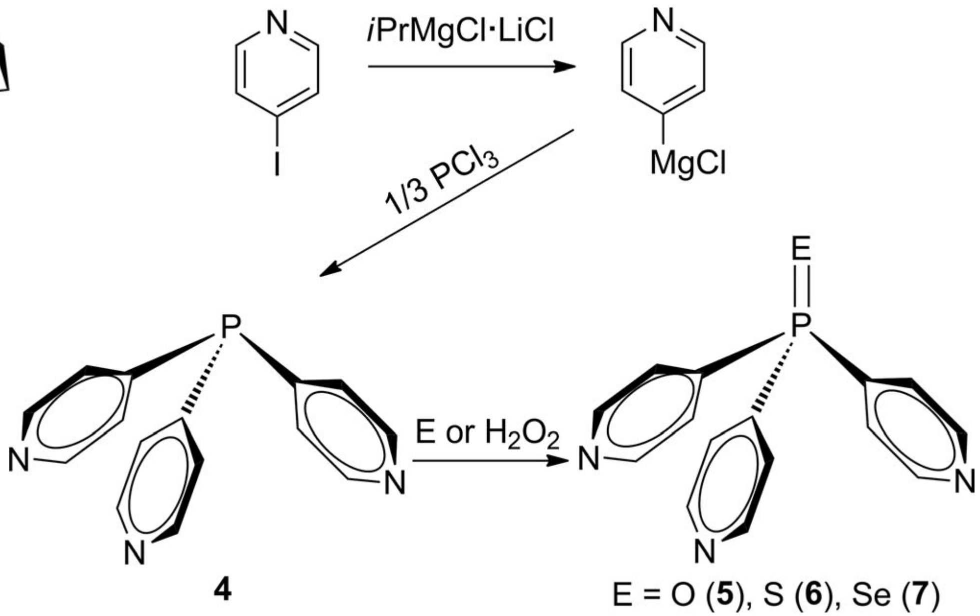
Major Scientific Results

❑ Syntheses of new triorganophosphine chalcogenides



Synthesis of tri(3-pyridyl)phosphine chalcogenides.

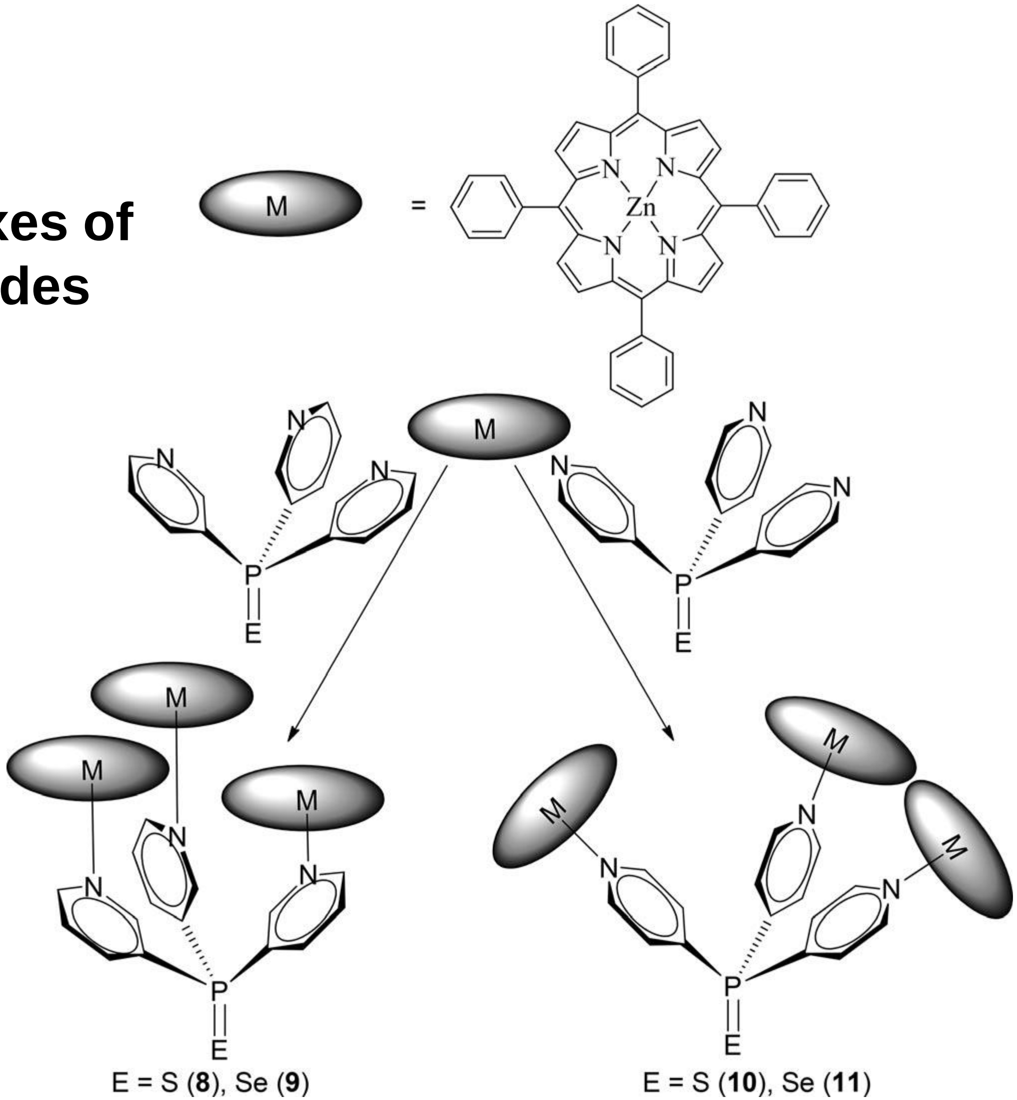
Synthesis of tri(4-pyridyl)phosphine chalcogenides.



L. Dubovan, A. Poellnitz, C. Silvestru, *Tris(3-pyridyl)- and tris(4-pyridyl)phosphine chalcogenides and their complexes with ZnTPP (TPP = tetraphenylporphyrinate), Eur. J. Inorg. Chem,.* **2016**, 1521–1527.

Major Scientific Results

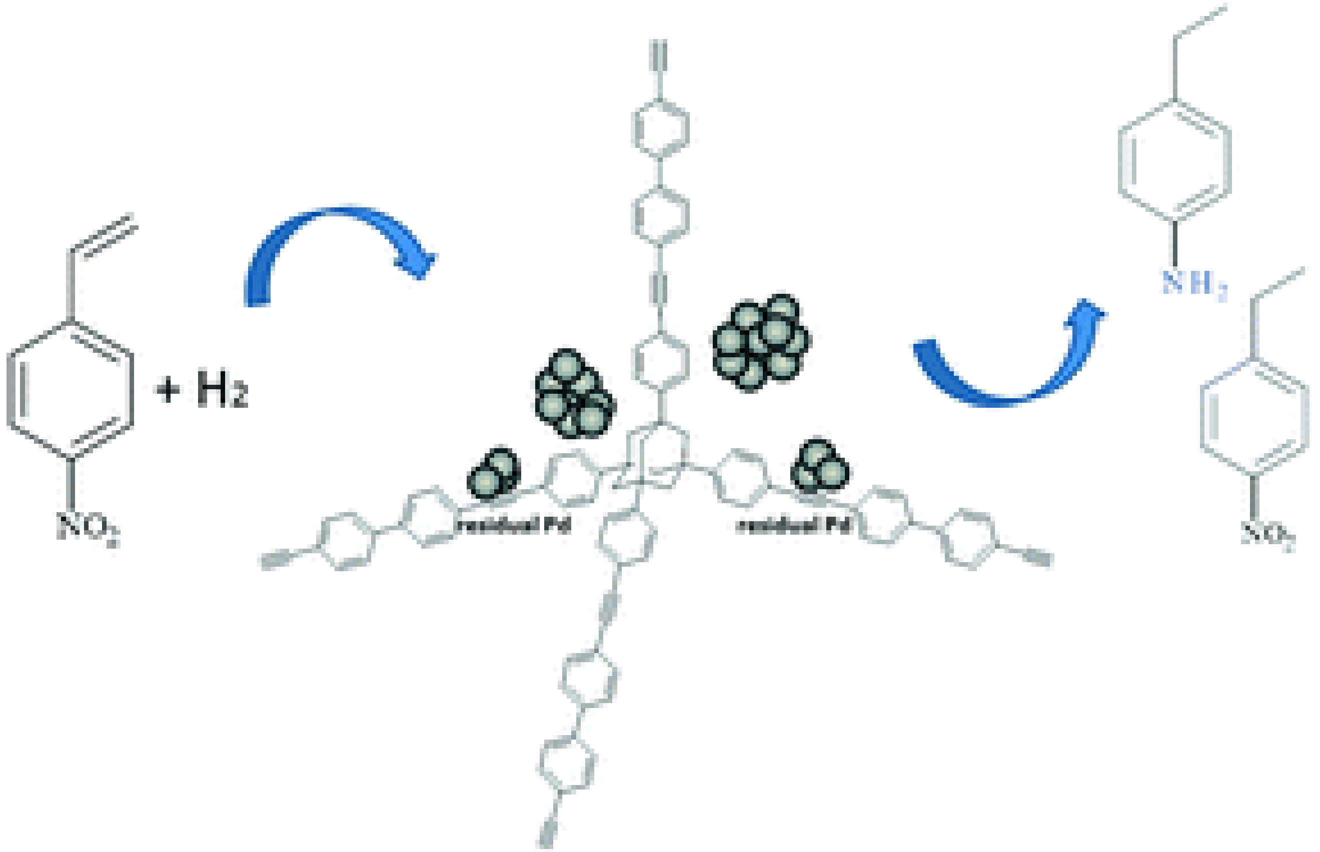
- ❑ **Syntheses of ZnTPP complexes of triorganophosphine chalcogenides 2, 3, 6, and 7.**



L. Dubovan, A. Poellnitz, C. Silvestru, *Tris(3-pyridyl)- and tris(4-pyridyl)phosphine chalcogenides and their complexes with ZnTPP (TPP = tetraphenylporphyrinate), Eur. J. Inorg. Chem,.* **2016**, 1521–1527.

Major Scientific Results

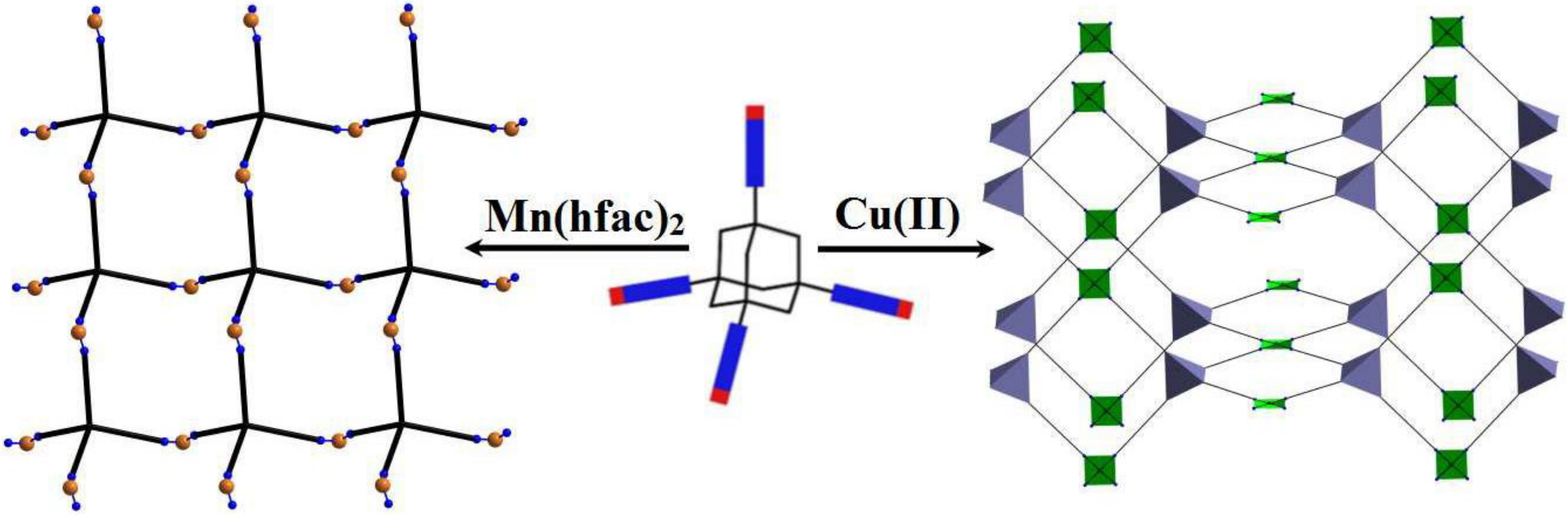
❑ **Syntheses of adamantane-based covalent–organic frameworks. Evaluation of their stability, adsorption capability, and behavior as catalysts.**



M. M. Trandafir, L. Pop, N. D. Hădade, M. Florea, F. Neațu, C. M. Teodorescu, B. Duraki, J. A. van Bokhoven, I. Grosu, V.I. Pârvulescu, H. Garcia, *Adamantane-based covalent–organic framework: stability, adsorption capability, and behaviour as catalyst and support for palladium and gold for the hydrogenation of nitrostyrene, Catal. Sci. Technol.*, **2016**, DOI: 10.1039/C6CY01631F.

Major Scientific Results

❑ Coordination polymers constructed from tetrahedral shaped adamantane tectons



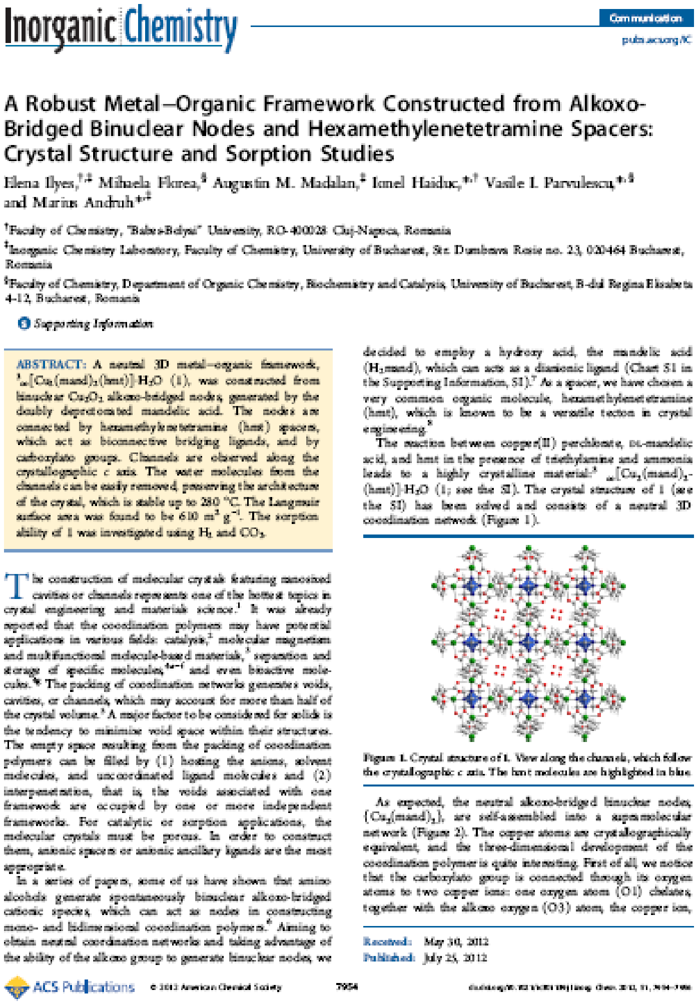
(1) **(2)**

Two rigid tetrahedral organic linkers derived from adamantane have been employed in constructing a 3-D, 4-fold interpenetrated framework featuring a PtS topology, $[\mathrm{CuL1(H_2O)_2](BF_4)_2\cdot 8H_2O}$ (2) (L1= 1,3,5,7-tetrakis{4-(4-pyridyl)phenyl}adamantane), and a 2-fold interpenetrated grid–like coordination polymer, $[\mathrm{Mn(hfac)_2(L2)_{0.5}}]$ (1) (L2= 1,3,5,7-tetrakis(4-cyano-phenyl)adamantane).

T. Mocanu, L. Pop, N.D. Hădade, S. Shova, I. Grosu, M. Andruh, *Coordination polymers constructed from tetrahedral shaped adamantane tectons, CrystEngComm*, DOI: 10.1039/C6CE02146H – accepted manuscript.

Dissemination of Results 2012

1. Ilyes, E.; Florea, M.; Madalan, A.M.; Haiduc, I.; Parvulescu, V.I.; Andruh, M., *A Robust Metal-Organic Framework Constructed from Alkoxo-Bridged Binuclear Nodes and Hexamethylenetetramine Spacers: Crystal Structure and Sorption Studies*, *Inorg. Chem*. **2012**, *51*, 7954-7956.



Inorganic Chemistry
Communication
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A Robust Metal–Organic Framework Constructed from Alkoxo-Bridged Binuclear Nodes and Hexamethylenetetramine Spacers: Crystal Structure and Sorption Studies

Elena Ilyes,[†,‡] Mihaela Florea,[§] Augustin M. Madalan,[‡] Ionel Haiduc,[*,†] Vasile I. Parvulescu,[*,§] and Marius Andruh[*,‡]

[†] Faculty of Chemistry, "Babes-Bolyai" University, RO-400028 Cluj-Napoca, Romania
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Supporting Information

ABSTRACT: A neutral 3D metal–organic framework, ${}^{3}_{\infty}[Cu_2(mand)_2(hmt)]\cdot H_2O$ (1), was constructed from binuclear Cu_2O_2 alkoxo-bridged nodes, generated by the doubly deprotonated mandelic acid. The nodes are connected by hexamethylenetetramine (hmt) spacers, which act as biconnective bridging ligands, and by carboxylato groups. Channels are observed along the crystallographic *c* axis. The water molecules from the channels can be easily removed, preserving the architecture of the crystal, which is stable up to 280 °C. The Langmuir surface area was found to be $610\ m^2\ g^{-1}$. The sorption ability of 1 was investigated using H_2 and CO_2.

The construction of molecular crystals featuring nanosized cavities or channels represents one of the hottest topics in crystal engineering and materials science.[1] It was already reported that the coordination polymers may have potential applications in various fields: catalysis,[2] molecular magnetism and multifunctional molecule-based materials,[3] separation and storage of specific molecules,[4a−f] and even bioactive molecules.[4g] The packing of coordination networks generates voids, cavities, or channels, which may account for more than half of the crystal volume.[5] A major factor to be considered for solids is the tendency to minimize void space within their structures. The empty space resulting from the packing of coordination polymers can be filled by (1) hosting the anions, solvent molecules, and uncoordinated ligand molecules and (2) interpenetration, that is, the voids associated with one framework are occupied by one or more independent frameworks. For catalytic or sorption applications, the molecular crystals must be porous. In order to construct them, anionic spacers or anionic ancillary ligands are the most appropriate.

In a series of papers, some of us have shown that amino alcohols generate spontaneously binuclear alkoxo-bridged cationic species, which can act as nodes in constructing mono- and bidimensional coordination polymers.[6] Aiming to obtain neutral coordination networks and taking advantage of the ability of the alkoxo group to generate binuclear nodes, we decided to employ a hydroxy acid, the mandelic acid (H_2mand), which can acts as a dianionic ligand (Chart S1 in the Supporting Information, SI).[7] As a spacer, we have chosen a very common organic molecule, hexamethylenetetramine (hmt), which is known to be a versatile tecton in crystal engineering.[8]

The reaction between copper(II) perchlorate, DL-mandelic acid, and hmt in the presence of triethylamine and ammonia leads to a highly crystalline material:[9] ${}_{\infty}[Cu_2(mand)_2(hmt)]\cdot H_2O$ (1; see the SI). The crystal structure of 1 (see the SI) has been solved and consists of a neutral 3D coordination network (Figure 1).

Figure 1. Crystal structure of 1. View along the channels, which follow the crystallographic *c* axis. The hmt molecules are highlighted in blue.

As expected, the neutral alkoxo-bridged binuclear nodes, $\{Cu_2(mand)_2\}$, are self-assembled into a supramolecular network (Figure 2). The copper atoms are crystallographically equivalent, and the three-dimensional development of the coordination polymer is quite interesting. First of all, we notice that the carboxylato group is connected through its oxygen atoms to two copper ions: one oxygen atom (O1) chelates, together with the alkoxo oxygen (O3) atom, the copper ion,

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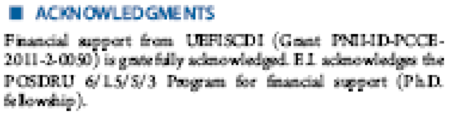
Published: July 25, 2012



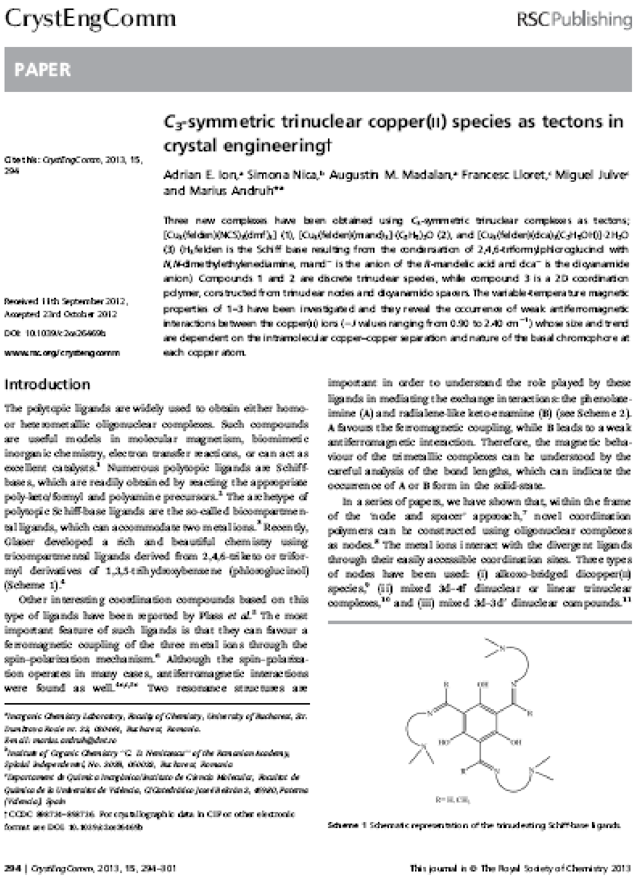
■ ACKNOWLEDGMENTS

Financial support from UEFISCDI (Grant PNII-ID-PCCE-2011-2-0050) is gratefully acknowledged. E.I. acknowledges the POSDRU 6/1.5/S/3 Program for financial support (Ph.D. fellowship).

Dissemination of Results 2013

2. Ion, A.E.; Nica, S.; Madalan, A.M.; Lloret, F.; Julve, M.; Andruh, M., *C_3-symmetric trinuclear copper(II) species as tectons in crystal engineering*, *CrystEngComm* **2013**, *15*, 294-301.

3. Circu, M.; Soran, A.; Hadade, N.D.; Rednic, M.; Terec, A.; Grosu, I. *Cryptands with 1,3,5-Tris(1',3'-Dioxan-2'-yl)-Benzene Units: Synthesis and Structural Investigations*, *J. Org. Chem.* **2013**, *78*, 8722-8729.



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PAPER

C_3-symmetric trinuclear copper(II) species as tectons in crystal engineering†

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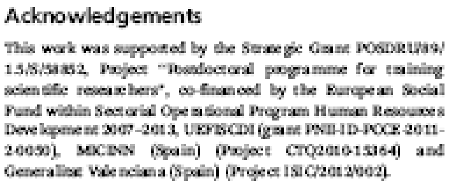
Introduction



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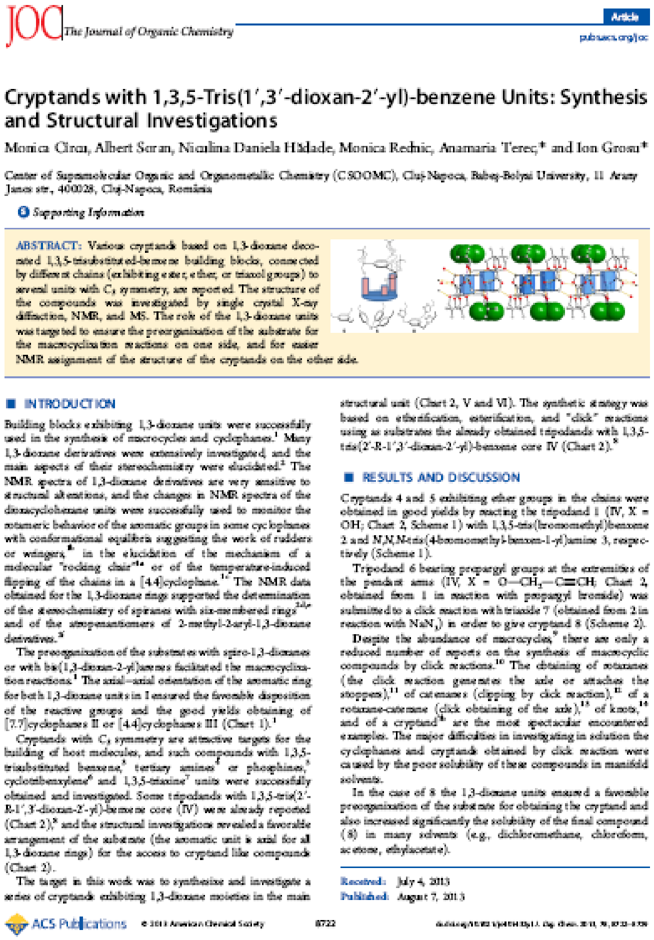

JOC The Journal of Organic Chemistry

Article

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Cryptands with 1,3,5-Tris(1′,3′-dioxan-2′-yl)-benzene Units: Synthesis and Structural Investigations

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Supporting Information

ABSTRACT: Various cryptands based on 1,3-dioxane decorated 1,3,5-trisubstituted-benzene building blocks, connected by different chains (exhibiting ester, ether, or triazol groups) to several units with C_3 symmetry, are reported. The structure of the compounds was investigated by single crystal X-ray diffraction, NMR, and MS. The role of the 1,3-dioxane units was targeted to ensure the preorganization of the substrate for the macrocyclization reactions on one side, and for easier NMR assignment of the structure of the cryptands on the other side.

INTRODUCTION

RESULTS AND DISCUSSION

ACKNOWLEDGMENTS

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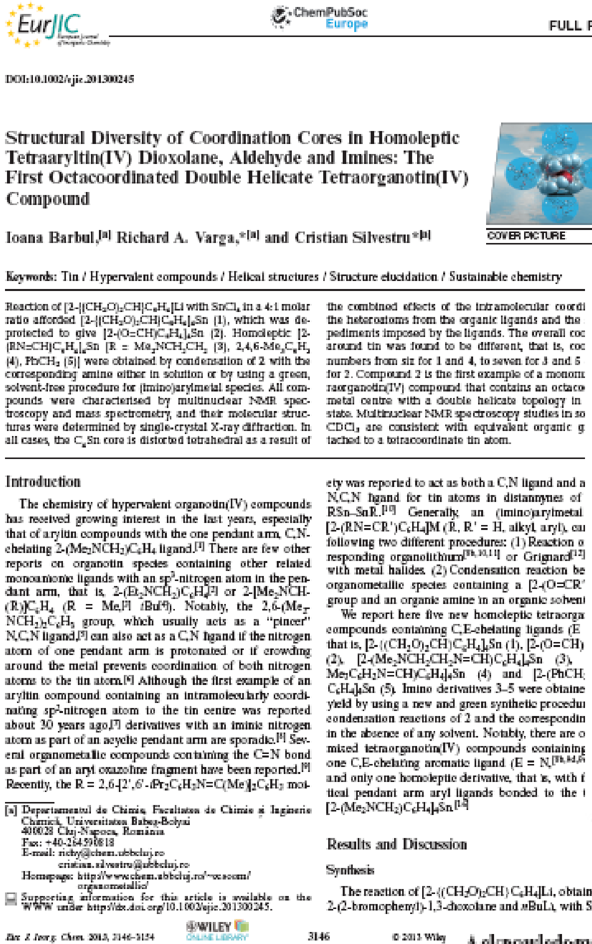
4. I. Barbul, R. A. Varga, C. Silvestru, *Structural diversity of coordination cores in new homoleptic tetraaryltin(IV) dioxolane, aldehyde and imines. The first octacoordinated double helicate tetraorganotin(IV) compound*, *Eur. J. Inorg. Chem*. **2013**, *18*, 3146-3154.
5. Candu, N.; Tudorache, M.; Florea, M.; Ilyes, E.; Vasiliu, F.; Mercioniu, I.; Coman, S.M.; Haiduc, I.; Andruh, M.; Parvulescu, V.I., *Postsynthetic modification of a Metal-Organic Framework (MOF) Structure for Enantioselective Catalytic Epoxidation*, *ChemPlusChem* **2013**, *78*, 443-450.



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Structural Diversity of Coordination Cores in Homoleptic Tetraaryltin(IV) Dioxolane, Aldehyde and Imines: The First Octacoordinated Double Helicate Tetraorganotin(IV) Compound

Ioana Barbul,[a] Richard A. Varga,*[a] and Cristian Silvestru*[a]

COVER PICTURE

Keywords: Tin / Hypervalent compounds / Helical structures / Structure elucidation / Sustainable chemistry

Reaction of $[2\text{-}\{(CH_2O)_2CH\}C_6H_4]Li$ with $SnCl_4$ in a 4:1 molar ratio afforded $[2\text{-}\{(CH_2O)_2CH\}C_6H_4]_4Sn$ (1), which was deprotected to give $[2\text{-}(O{=}CH)C_6H_4]_4Sn$ (2). Homoleptic $[2\text{-}(RN{=}CH)C_6H_4]_4Sn$ [R = $Me_2NCH_2CH_2$ (3), 2,4,6-$Me_3C_6H_2$ (4), $PhCH_2$ (5)] were obtained by condensation of 2 with the corresponding amine either in solution or by using a green, solvent-free procedure for (imino)arylmetal species. All compounds were characterised by multinuclear NMR spectroscopy and mass spectrometry, and their molecular structures were determined by single-crystal X-ray diffraction. In all cases, the C_4Sn core is distorted tetrahedral as a result of the combined effects of the intramolecular coordi the heteroatoms from the organic ligands and the pediments imposed by the ligands. The overall coc around tin was found to be different, that is, coc numbers from six for 1 and 4, to seven for 3 and 5 for 2. Compound 2 is the first example of a monom raorganotin(IV) compound that contains an octaco metal centre with a double helicate topology in state. Multinuclear NMR spectroscopy studies in so $CDCl_3$ are consistent with equivalent organic g tached to a tetracoordinate tin atom.

Introduction

The chemistry of hypervalent organotin(IV) compounds has received growing interest in the last years, especially that of aryltin compounds with the one pendant arm, C,N-chelating 2-(Me_2NCH_2)C_6H_4 ligand.[1] There are few other reports on organotin species containing other related monoanionic ligands with an sp^3-nitrogen atom in the pendant arm, that is, 2-(Et_2NCH_2)C_6H_4[2] or 2-[Me_2NCH(R)]C_6H_4 (R = Me,[3] *t*Bu[4]). Notably, the 2,6-(Me_2NCH_2)$_2C_6H_3$ group, which usually acts as a "pincer" N,C,N ligand,[5] can also act as a C,N ligand if the nitrogen atom of one pendant arm is protonated or if crowding around the metal prevents coordination of both nitrogen atoms to the tin atom.[6] Although the first example of an aryltin compound containing an intramolecularly coordinating sp^2-nitrogen atom to the tin centre was reported about 30 years ago,[7] derivatives with an iminic nitrogen atom as part of an acyclic pendant arm are sporadic.[8] Several organometallic compounds containing the C=N bond as part of an aryl oxazoline fragment have been reported.[9] Recently, the R = 2,6-[2′,6′-$iPr_2C_6H_3N{=}C(Me)$]$_2C_6H_3$ moiety was reported to act as both a C,N ligand and a N,C,N ligand for tin atoms in distannynes of RSn–SnR.[10] Generally, an (imino)arylmetal [2-(RN=CR′)C_6H_4]M (R, R′ = H, alkyl, aryl), ca following two different procedures: (1) Reaction o responding organolithium[8b,10,11] or Grignard[12] with metal halides. (2) Condensation reaction be organometallic species containing a [2-(O=CR′ group and an organic amine in an organic solvent

We report here five new homoleptic tetraorga compounds containing C,E-chelating ligands (E that is, [2-{(CH_2O)$_2$CH}C_6H_4]$_4$Sn (1), [2-(O=CH) (2), [2-($Me_2NCH_2CH_2N{=}CH$)C_6H_4]$_4$Sn (3), $Me_3C_6H_2N{=}CH$)C_6H_4]$_4$Sn (4) and [2-(PhCH C_6H_4]$_4$Sn (5). Imino derivatives 3–5 were obtaine yield by using a new and green synthetic procedu condensation reactions of 2 and the correspondin in the absence of any solvent. Notably, there are o mixed tetraorganotin(IV) compounds containing one C,E-chelating aromatic ligand (E = N,[8b,8d,8 and only one homoleptic derivative, that is, with t tical pendant arm aryl ligands bonded to the [2-(Me_2NCH_2)C_6H_4]$_4$Sn.[14]

Results and Discussion

Synthesis

The reaction of [2-{(CH_2O)$_2$CH}C_6H_4]Li, obtained from 2-(2-bromophenyl)-1,3-dioxolane and *n*BuLi, with $SnCl_4$ af-

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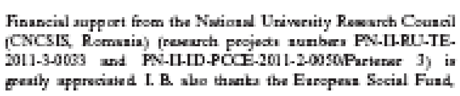

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Postsynthetic Modification of a Metal–Organic Framework (MOF) Structure for Enantioselective Catalytic Epoxidation

Natalia Candu,[a] Mădălina Tudorache,[a] Mihaela Florea,[a] Elena Ilyes,[b] Florin Vasiliu,[d] Ionel Mercioniu,[d] Simona M. Coman,*[a] Ionel Haiduc,[b] Marius Andruh,[c] and Vasile I. Pârvulescu*[a]

Postsynthetic modification of [Cu_2(mand)$_2$(hmt)] (mand = mandelic acid, hmt = hexamethylenetetramine) with a chiral, dimeric chromium(III)–salen complex led to a robust structure. Characterization of this new material showed that it perfectly preserved the textural and structural properties of the parent metal–organic framework (MOF). Although epoxidation of *trans*-methyl cinnamate with hydrogen peroxide led to copper leaching of 2–3%, experiments performed with *N*-methylmorpholine-*N*-oxide indicated no leaching, even after 72 h of exposure. The obtained chiral MOF is an effective catalyst for the enantioselective epoxidation of *trans*-methyl cinnamate and leads to (2*R*,3*S*)-phenylglycidate with a high enantiomeric excess at room temperature.

Introduction

One of the most important transformations in asymmetric catalysis is the epoxidation of C=C bond, which provides access to enantiomerically enriched epoxides as intermediates in the production of pharmaceuticals. For example, the C_{13} side chain of drugs such as Taxol[1,2] can be prepared from the valuable (2*R*,3*S*)-phenylglycidate intermediate. At the industrial level, its production consists of the enzymatic kinetic resolution of (±)-phenylglycidate racemates.[3] Unfortunately, this method suffers from several drawbacks. The most important of which is the poor yield (42%) of (2*R*,3*S*)-phenylglycidate that arises from the unwanted enantiomer, (2*S*,3*R*)-phenylglycidate; this generates large amounts of waste (ca. 200 tons per year). Catalytic asymmetric synthesis of (2*R*,3*S*)-phenylglycidate is therefore highly desirable. For such a purpose, the asymmetric epoxidation (AE) and asymmetric dihydroxylation (AD) of *cis*-methyl cinnamates are among the most important methodologies developed.[4–8] AE provides chiral glycidates in a single step, and therefore, is considered to be a more efficient route than that of AD.

Studies in this area have shown that manganese–salen complexes display high enantioselectivities in the epoxidation of *Z* (*cis*) alkenes,[9] but do not eliminate difficulties in the synthesis of *cis*-cinnamic esters.[9] On the other hand, homogeneous chiral organometallic complexes, often prepared from challenging and expensive ligands, are mainly undesired at the end of the synthesis, and therefore, are considered to be pollutants that must be separated from the desired product. They are also in a clear contradiction to the principles of green chemistry, which encourage the design of processes that minimize the generation of by-products. Therefore, a much better solution would be to use heterogeneous catalysts. In this context, making chiral coordination compounds insoluble, and consequently easy to recover and reuse, is a logical way to answer the principles of green chemistry and sustainable development.

These facts prompted us 1) to search for methods to synthesize methyl (2*R*,3*S*)-phenylglycidates through the catalytic AE of commercially available and inexpensive *trans*-methyl cinnamate and 2) to synthesize novel heterogeneous chiral coordination compounds. In this context, we previously reported a heterogeneous, chiral, dimeric Cr^{III}–salen complex prepared through a grafting methodology that involved an aminopropyl-functionalized silica.[10] The catalysts obtained were active and highly enantioselective for the transformation of *trans*-methyl cinnamate into methyl (2*R*,3*S*)-2,3-dihydroxy-3-phenylpropionate through consecutive epoxidation/epoxide ring-opening reactions.

Although the grafting methodology of chiral complexes is not new, the enantiomeric excess (*ee*) values achieved to date have frequently been rather modest compared with homogeneous conditions and there is not yet a clear understanding of

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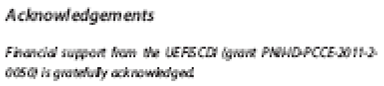

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6. Tudor, V.; Mocanu, T.; Tuna, F.; Madalan, A.M.; Maxim, C.; Shova, S.; Andruh, M., *Mixed ligand binuclear alkoxo-bridged copper(II) complexes derived from aminoalcohols and nitrogen ligands*, *J. Molec. Struct*. **2013**, *1046*, 164-170.
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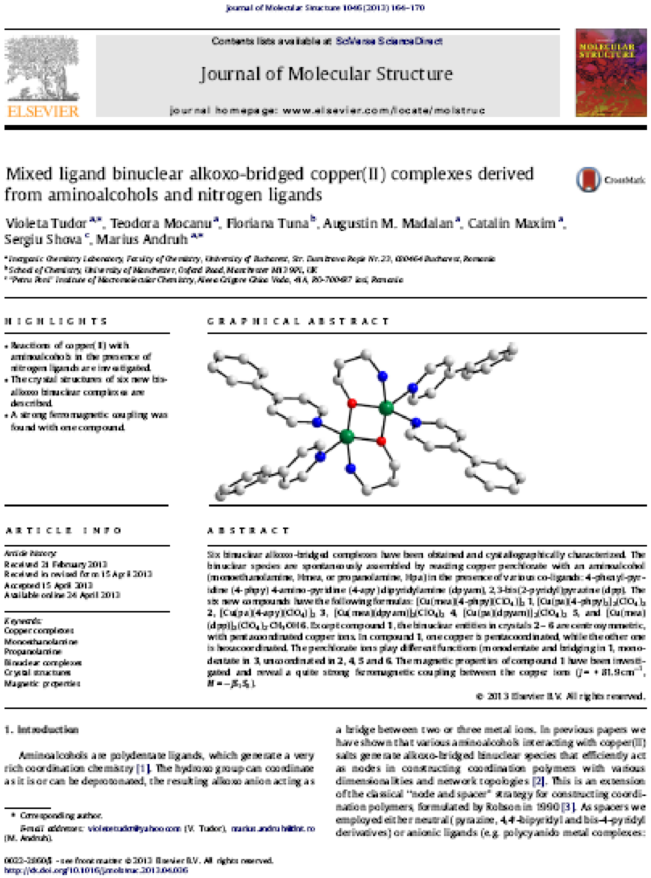

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Mixed ligand binuclear alkoxo-bridged copper(II) complexes derived from aminoalcohols and nitrogen ligands

Violeta Tudor [a,*], Teodora Mocanu [a], Floriana Tuna [b], Augustin M. Madalan [a], Catalin Maxim [a], Sergiu Shova [c], Marius Andruh [a,*]

HIGHLIGHTS

GRAPHICAL ABSTRACT

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ABSTRACT

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1. Introduction

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Di(imino)aryltin(IV) dichlorides as tectons for heterometallic coordination compounds†

Ioana Barbul,[a] Richard A. Varga,*[a] Kieran C. Molloy[b] and Cristian Silvestru*[a]

Introduction

Results and discussion

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Dalton Trans., 2013, 42, 15427–15436 | 15427

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8. Alexandru, M.-G.; Visinescu, D.; Shova, S.; Lloret, F.; Julve, M.; Andruh, M., *Two-Dimensional Coordination Polymers Constructed by [Ni^{II}Ln^{III}] Nodes and [W^{IV}(bpy)(CN)$_6$]$^{2-}$ Spacers: A Network of [Ni^{II}Dy^{III}] Single Molecule Magnet*, *Inorg. Chem*. **2013**, *52*, 11627-11637.

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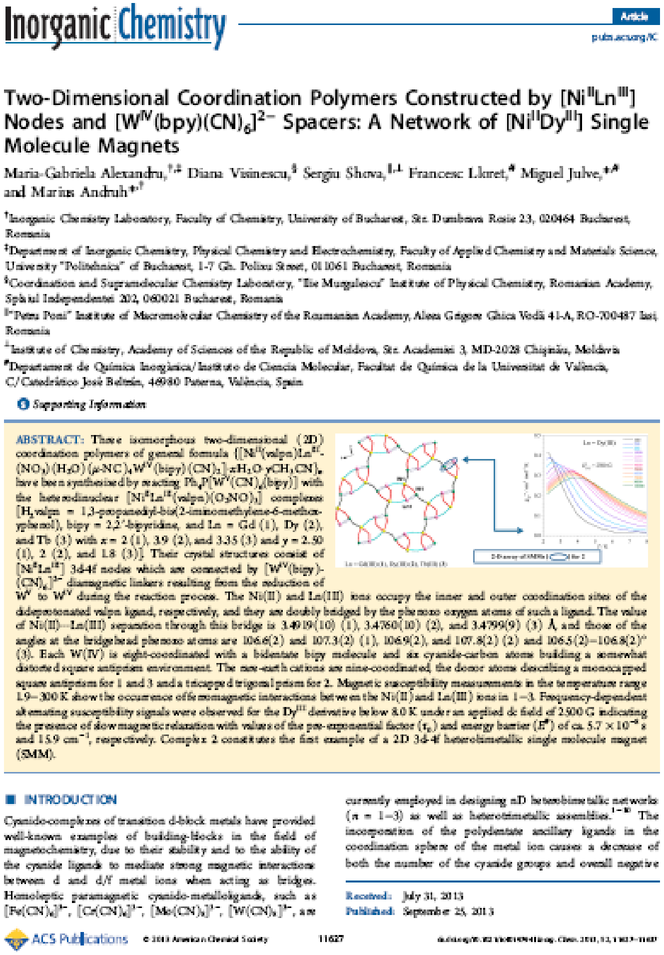

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Two-Dimensional Coordination Polymers Constructed by [Ni^{II}Ln^{III}] Nodes and [W^{IV}(bpy)(CN)$_6$]$^{2-}$ Spacers: A Network of [Ni^{II}Dy^{III}] Single Molecule Magnets

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Supporting Information

ABSTRACT: Three isomorphous two-dimensional (2D) coordination polymers of general formula $\{[Ni^{II}(valpn)Ln^{III}(NO_3)(H_2O)(\mu\text{-}NC)_4W^{IV}(bipy)(CN)_2]\cdot xH_2O\cdot yCH_3CN\}_n$ have been synthesized by reacting $Ph_4P[W^{V}(CN)_6(bipy)]$ with the heterodinuclear $[Ni^{II}Ln^{III}(valpn)(O_2NO)_3]$ complexes [H_2valpn = 1,3-propanediyl-bis(2-iminomethylene-6-methoxyphenol), bipy = 2,2′-bipyridine, and Ln = Gd (1), Dy (2), and Tb (3) with x = 2 (1), 3.9 (2), and 3.35 (3) and y = 2.50 (1), 2 (2), and 1.8 (3)]. Their crystal structures consist of $[Ni^{II}Ln^{III}]$ 3d-4f nodes which are connected by $[W^{IV}(bipy)(CN)_6]^{2-}$ diamagnetic linkers resulting from the reduction of W^{V} to W^{IV} during the reaction process. The Ni(II) and Ln(III) ions occupy the inner and outer coordination sites of the dideprotonated valpn ligand, respectively, and they are doubly bridged by the phenoxo oxygen atoms of such a ligand. The value of Ni(II)···Ln(III) separation through this bridge is 3.4919(10) (1), 3.4760(10) (2), and 3.4799(9) (3) Å, and those of the angles at the bridgehead phenoxo atoms are 106.6(2) and 107.3(2) (1), 106.9(2), and 107.8(2) (2) and 106.5(2)−106.8(2)° (3). Each W(IV) is eight-coordinated with a bidentate bipy molecule and six cyanide-carbon atoms building a somewhat distorted square antiprism environment. The rare-earth cations are nine-coordinated, the donor atoms describing a monocapped square antiprism for 1 and 3 and a tricapped trigonal prism for 2. Magnetic susceptibility measurements in the temperature range 1.9−300 K show the occurrence of ferromagnetic interactions between the Ni(II) and Ln(III) ions in 1−3. Frequency-dependent alternating susceptibility signals were observed for the Dy^{III} derivative below 8.0 K under an applied dc field of 2500 G indicating the presence of slow magnetic relaxation with values of the pre-exponential factor (τ_0) and energy barrier (E^{a}) of ca. 5.7×10^{-8} s and 15.9 cm^{-1}, respectively. Complex 2 constitutes the first example of a 2D 3d-4f heterobimetallic single molecule magnet (SMM).

INTRODUCTION

Cyanido-complexes of transition d-block metals have provided well-known examples of building-blocks in the field of magnetochemistry, due to their stability and to the ability of the cyanide ligands to mediate strong magnetic interactions between d and d/f metal ions when acting as bridges. Homoleptic paramagnetic cyanido-metalloligands, such as $[Fe(CN)_6]^{3-}$, $[Cr(CN)_6]^{3-}$, $[Mo(CN)_8]^{3-}$, $[W(CN)_8]^{3-}$, are currently employed in designing nD heterobimetallic networks (n = 1−3) as well as heterotrimetallic assemblies.[1−10] The incorporation of the polydentate ancillary ligands in the coordination sphere of the metal ion causes a decrease of both the number of the cyanide groups and overall negative

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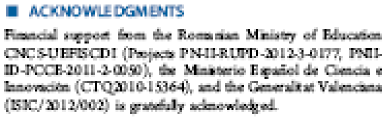

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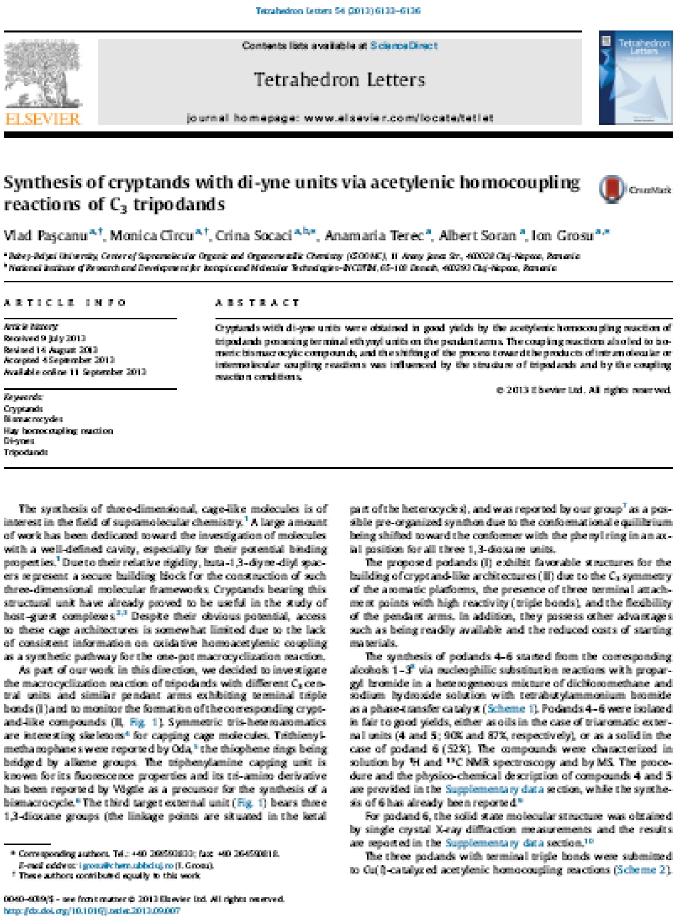

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Synthesis of cryptands with di-yne units via acetylenic homocoupling reactions of C_3 tripodands

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ABSTRACT

Cryptands with di-yne units were obtained in good yields by the acetylenic homocoupling reaction of tripodands possessing terminal ethynyl units on the pendant arms. The coupling reactions also led to isomeric bismacrocyclic compounds, and the shifting of the process toward the products of intramolecular or intermolecular coupling reactions was influenced by the structure of tripodands and by the coupling reaction conditions.

The synthesis of three-dimensional, cage-like molecules is of interest in the field of supramolecular chemistry.[1] A large amount of work has been dedicated toward the investigation of molecules with a well-defined cavity, especially for their potential binding properties.[1] Due to their relative rigidity, buta-1,3-diyne-diyl spacers represent a secure building block for the construction of such three-dimensional molecular frameworks. Cryptands bearing this structural unit have already proved to be useful in the study of host–guest complexes.[2,3] Despite their obvious potential, access to these cage architectures is somewhat limited due to the lack of consistent information on oxidative homoacetylenic coupling as a synthetic pathway for the one-pot macrocyclization reaction.

As part of our work in this direction, we decided to investigate the macrocyclization reaction of tripodands with different C_3 central units and similar pendant arms exhibiting terminal triple bonds (I) and to monitor the formation of the corresponding cryptand-like compounds (II, Fig. 1). Symmetric tris-heteroaromatics are interesting skeletons[4] for capping cage molecules. Trithienylmethanophanes were reported by Oda,[5] the thiophene rings being bridged by alkene groups. The triphenylamine capping unit is known for its fluorescence properties and its tri-amino derivative has been reported by Vögtle as a precursor for the synthesis of a bismacrocycle.[6] The third target external unit (Fig. 1) bears three 1,3-dioxane groups (the linkage points are situated in the ketal part of the heterocycles), and was reported by our group[7] as a possible pre-organized synthon due to the conformational equilibrium being shifted toward the conformer with the phenyl ring in an axial position for all three 1,3-dioxane units.

The proposed podands (I) exhibit favorable structures for the building of cryptand-like architectures (II) due to the C_3 symmetry of the aromatic platforms, the presence of three terminal attachment points with high reactivity (triple bonds), and the flexibility of the pendant arms. In addition, they possess other advantages such as being readily available and the reduced costs of starting materials.

The synthesis of podands 4–6 started from the corresponding alcohols 1–3[8] via nucleophilic substitution reactions with propargyl bromide in a heterogeneous mixture of dichloromethane and sodium hydroxide solution with tetrabutylammonium bromide as a phase-transfer catalyst (Scheme 1). Podands 4–6 were isolated in fair to good yields, either as oils in the case of triaromatic external units (4 and 5; 90% and 87%, respectively), or as a solid in the case of podand 6 (52%). The compounds were characterized in solution by ^1H and ^{13}C NMR spectroscopy and by MS. The procedure and the physico-chemical description of compounds 4 and 5 are provided in the Supplementary data section, while the synthesis of 6 has already been reported.[9]

For podand 6, the solid state molecular structure was obtained by single crystal X-ray diffraction measurements and the results are reported in the Supplementary data section.[10]

The three podands with terminal triple bonds were submitted to Cu(I)-catalyzed acetylenic homocoupling reactions (Scheme 2).

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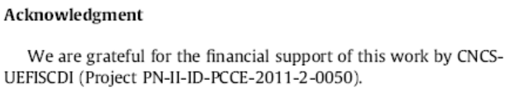

Acknowledgment

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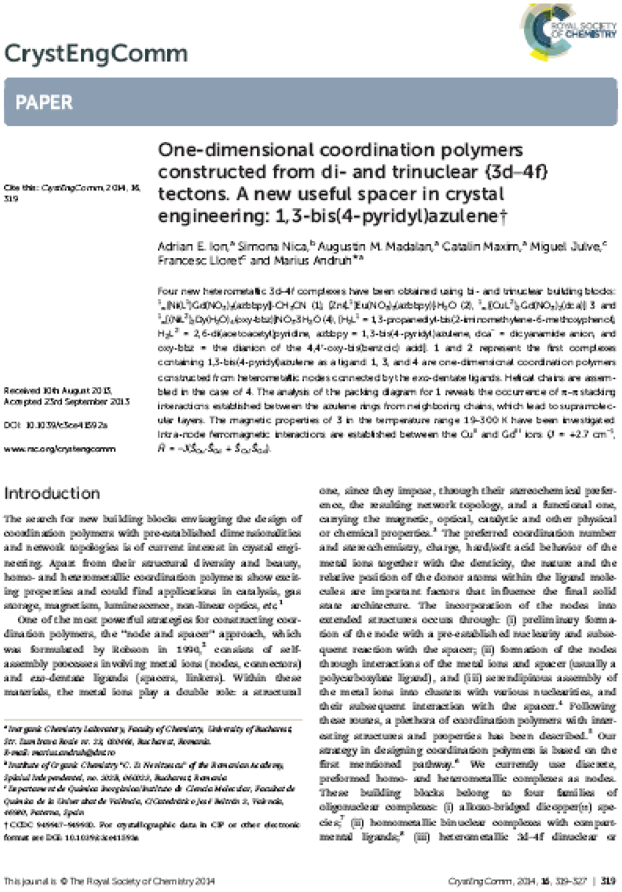
Dissemination of Results 2014

10. Ion, A.E.; Nica, S.; Madalan, A.M.; Maxim, C.; Julve, M.; Lloret, F.; Andruh, M., *One-dimensional coordination polymers constructed from di- and trinuclear {3d–4f} tectons. A new useful spacer in crystal engineering: 1,3-bis(4-pyridyl)azulene*, *CrystEngComm* **2014**, *15*, 319-327.



CrystEngComm

ROYAL SOCIETY OF CHEMISTRY

PAPER

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One-dimensional coordination polymers constructed from di- and trinuclear {3d–4f} tectons. A new useful spacer in crystal engineering: 1,3-bis(4-pyridyl)azulene†

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Four new heterometallic 3d–4f complexes have been obtained using bi- and trinuclear building blocks: ${}^1_\infty[NiL^1Gd(NO_3)_3(azbpy)]\cdot CH_3CN$ (1), $[ZnL^1Eu(NO_3)_3(azbpy)]\cdot H_2O$ (2), ${}^1_\infty[(CuL^2)_2Gd(NO_3)_2(dca)]$ 3 and ${}^1_\infty[(NiL^2)_2Dy(H_2O)_4(oxy\text{-}bbz)](NO_3)\cdot 3H_2O$ (4), (H_2L^1 = 1,3-propanediyl-bis(2-iminomethylene-6-methoxyphenol), H_2L^2 = 2,6-di(acetoacetyl)pyridine, azbpy = 1,3-bis(4-pyridyl)azulene, dca^- = dicyanamide anion, and oxy-bbz = the dianion of the 4,4′-oxy-bis(benzoic) acid). 1 and 2 represent the first complexes containing 1,3-bis(4-pyridyl)azulene as a ligand. 1, 3, and 4 are one-dimensional coordination polymers constructed from heterometallic nodes connected by the exo-dentate ligands. Helical chains are assembled in the case of 4. The analysis of the packing diagram for 1 reveals the occurrence of π–π stacking interactions established between the azulene rings from neighboring chains, which lead to supramolecular layers. The magnetic properties of 3 in the temperature range 1.9–300 K have been investigated. Intra-node ferromagnetic interactions are established between the Cu^{II} and Gd^{III} ions (J = +2.7 cm^{-1}, $\hat{H} = -J(\hat{S}_{Cu1}\cdot\hat{S}_{Gd} + \hat{S}_{Cu2}\cdot\hat{S}_{Gd})$).

Introduction

The search for new building blocks envisaging the design of coordination polymers with pre-established dimensionalities and network topologies is of current interest in crystal engineering. Apart from their structural diversity and beauty, homo- and heterometallic coordination polymers show exciting properties and could find applications in catalysis, gas storage, magnetism, luminescence, non-linear optics, *etc.*[1]

One of the most powerful strategies for constructing coordination polymers, the "node and spacer" approach, which was formulated by Robson in 1990,[2] consists of self-assembly processes involving metal ions (nodes, connectors) and exo-dentate ligands (spacers, linkers). Within these materials, the metal ions play a double role: a structural one, since they impose, through their stereochemical preference, the resulting network topology, and a functional one, carrying the magnetic, optical, catalytic and other physical or chemical properties.[3] The preferred coordination number and stereochemistry, charge, hard/soft acid behavior of the metal ions together with the denticity, the nature and the relative position of the donor atoms within the ligand molecules are important factors that influence the final solid state architecture. The incorporation of the nodes into extended structures occurs through: (i) preliminary formation of the node with a pre-established nuclearity and subsequent reaction with the spacer; (ii) formation of the nodes through interactions of the metal ions and spacer (usually a polycarboxylate ligand), and (iii) serendipitous assembly of the metal ions into clusters with various nuclearities, and their subsequent interaction with the spacer.[4] Following these routes, a plethora of coordination polymers with interesting structures and properties has been described.[5] Our strategy in designing coordination polymers is based on the first mentioned pathway.[6] We currently use discrete, preformed homo- and heterometallic complexes as nodes. These building blocks belong to four families of oligonuclear complexes: (i) alkoxo-bridged dicopper(II) species;[7] (ii) homometallic binuclear complexes with compartmental ligands;[8] (iii) heterometallic 3d–4f dinuclear or

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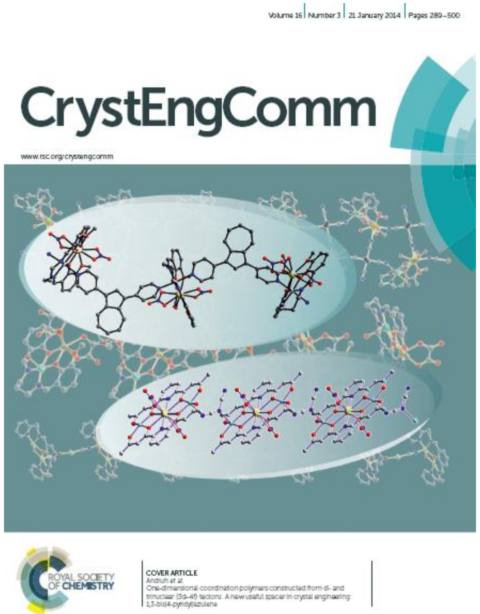
† CCDC 949947–949950. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ce41592a



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ROYAL SOCIETY OF CHEMISTRY

COVER ARTICLE
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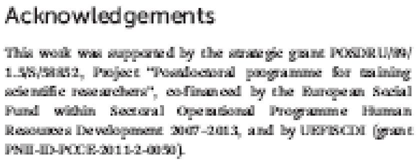
One-dimensional coordination polymers constructed from di- and trinuclear {3d–4f} tectons. A new useful spacer in crystal engineering: 1,3-bis(4-pyridyl)azulene



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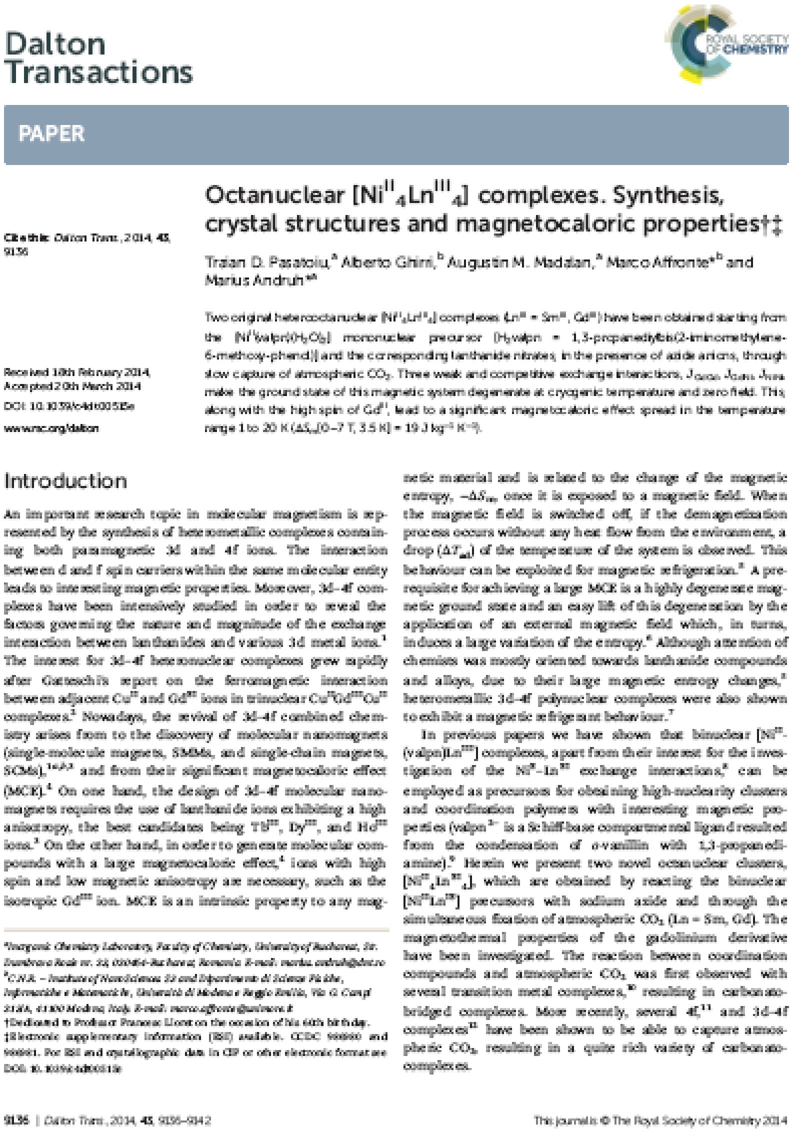
Dissemination of Results 2014

11. Pasatoiu, T.D.; Ghirri, A.; Madalan, A.M.; Affronte, M.; Andruh, M., Octanuclear [$Ni^{II}_4Ln^{III}_4$] complexes. Synthesis, crystal structures and magnetocaloric properties *with 1,3,5-Tris(1',3'-Dioxan-2'-yl)-Benzene Units: Synthesis and Structural Investigations, Dalton Trans.* **2014**, *43*, 9136-9142.



Dalton Transactions

PAPER

Octanuclear [$Ni^{II}_4Ln^{III}_4$] complexes. Synthesis, crystal structures and magnetocaloric properties†‡

Traian D. Pasatoiu,[a] Alberto Ghirri,[b] Augustin M. Madalan,[a] Marco Affronte*[b] and Marius Andruh*[a]

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Two original heterooctanuclear [$Ni^{II}_4Ln^{III}_4$] complexes ($Ln^{III} = Sm^{III}, Gd^{III}$) have been obtained starting from the [$Ni^{II}(valpn)(H_2O)_2$] mononuclear precursor (H_2valpn = 1,3-propanediylbis(2-iminomethylene-6-methoxy-phenol)) and the corresponding lanthanide nitrates, in the presence of azide anions, through slow capture of atmospheric CO_2. Three weak and competitive exchange interactions, J_{GdGd}, J_{GdNi}, J_{NiNi}, make the ground state of this magnetic system degenerate at cryogenic temperature and zero field. This, along with the high spin of Gd^{III}, lead to a significant magnetocaloric effect spread in the temperature range 1 to 20 K (ΔS_m[0–7 T, 3.5 K] = 19 J kg^{-1} K^{-1}).

Introduction

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Dissemination of Results 2015

12. Dumbrava, A.; Olar, R.; Badea, M.; Maxim, C.; Ghica, D. Andruh, M., *New coordination polymers with chromato bridges: 1∞[Ni(phen)(H2O)2(m-O2CrO2)] and 3∞[Mn(4,4'-bipy)(H2O)(m-O3CrO)]·H2O* **,** *Inorg. Chim. Acta*, **2015**, *426*, 50-54.

13. A.E. Ghionoiu, D.L. Popescu, C. Maxim, A.M. Madalan, I. Haiduc, M.Andruh, *Atmospheric CO_2 capture by a triphenyltin–1,2-bis(4-pyridyl)ethane system with formation of a rare trinuclear carbonato-centered core*, *Inorg. Chem. Comm.*, **2015**, *58,* 71-73.

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New coordination polymers with chromato bridges: $^{1}_{\infty}[Ni(phen)(H_2O)_2(\mu\text{-}O_2CrO_2)]$ and $^{3}_{\infty}[Mn(4,4'\text{-}bipy)(H_2O)(\mu\text{-}O_3CrO)]\cdot H_2O$

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ABSTRACT

Two new coordination polymers have been assembled using the chromato ions as bridging ligands: $^{1}_{\infty}[Ni(phen)(H_2O)_2(\mu\text{-}O_2CrO_2)]$ **1**, and $^{3}_{\infty}[Mn(4,4'\text{-}bipy)(H_2O)(\mu\text{-}O_3CrO)]\cdot H_2O$ **2**. In crystal **1** the chromate ions act as bridges connecting two nickel ions through two oxygen atoms, resulting in infinite chains. 1,10-Phenanthroline acts as a blocking ligand. In compound **2**, each chromato ion is connected to three manganese ions, resulting in layers which are parallel to the *ab* plane. The layers are constructed from $\{Mn_3Cr_3\}$ meshes, each metal atom being shared between three other meshes. The structure is expanded into the third direction by connecting the inorganic layers through 4,4'-bipy spacers. The thermal decomposition of the two compounds has been investigated.

1. Introduction

The chromate anion, CrO_4^{2-}, has a quite rich coordination chemistry. It can act as a terminal ligand, through one oxygen atom, or as a bridge, involving in the interaction with the metal ion two, three or all the oxygen atoms [1]. In the last cases, either oligonuclear complexes or coordination polymers can be assembled. The interest in this chemistry is due to several reasons: (i) chromium(VI) compounds are known to rise important ecological problems, showing a strong mutagenic effect [2]; (ii) the various bridging modes of the chromate anion affords coordination polymers with relevance in crystal engineering; (iii) some complexes of transition metal ions with chromato ligands are useful precursors for obtaining mixed metal oxides [3], or mixtures of oxides, which can be used as catalysts [4]. The chromato-bridged polynuclear complexes are assembled by reacting transition metal ions with a soluble chromate (usually of sodium, potassium, or ammonium) with or without additional chelating or bridging ligands. Generally, the chelating (blocking) ligands are employed to obtain discrete species and 1-D coordination polymers. For example, the reaction between the mononuclear complex $[LFeCl_3]$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononanine) and $(NH_4)_2CrO_4$ lead to a binuclear complexes with triple chromato bridges connecting the iron(III) ions [5]; a tetranuclear complex, $[\{Cu(2,2'\text{-}bipy)_2\}_3(\mu\text{-}CrO_4)](ClO_4)_4\cdot H_2O$, has been obtained by reacting potassium chromate with copper(II) perchlorate and 2,2'-bipyridine, the chromato ion being linked to three copper(II) ions [6]. Interestingly, by replacing 2,2'-bipyridine with 1,10-phenanthroline, a binuclear complex [Cu(II)Cr(VI)] complex with monodentate chromate was obtained [7]. In principle, if only one bidentate chelating ligand or a macrocycle is attached to the assembling cation, the formation of 1-D coordination polymers is favored. A nice example is the chain resulted by connecting the $\{Ni(MAC)\}^{2+}$ complex cations with chromato bridges (MAC = 2,5,9,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane) [8]. Conversely, 2-D and 3-D coordination polymers can be constructed using divergent (*exo*-dentate) ligands. One of the most popular bridging ligand in crystal engineering is 4,4'-bipyridine [9]. Herein we report on two new chromato-bridged coordination polymers, constructed using nickel(II) and manganese(II) as assembling cations, in the presence of 1,10-phenathroline (phen) and, respectively, 4,4'-bipyridine (4,4'-bipy).

2. Experimental part

2.1. Materials and physical measurements

Nickel(II) acetate tetrahydrate, manganese(II) acetate tetrahydrate, sodium chromate, 1,10-phenathroline monohydrate, and

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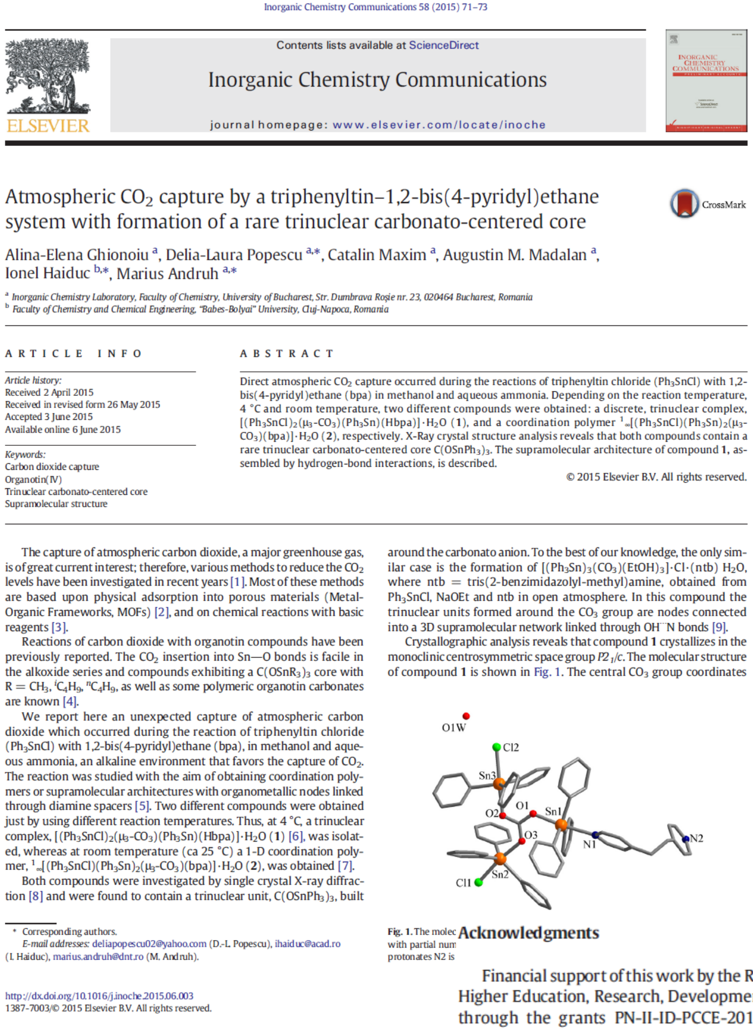

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Atmospheric CO_2 capture by a triphenyltin–1,2-bis(4-pyridyl)ethane system with formation of a rare trinuclear carbonato-centered core

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ABSTRACT

Direct atmospheric CO_2 capture occurred during the reactions of triphenyltin chloride (Ph_3SnCl) with 1,2-bis(4-pyridyl)ethane (bpa) in methanol and aqueous ammonia. Depending on the reaction temperature, 4 °C and room temperature, two different compounds were obtained: a discrete, trinuclear complex, $[(Ph_3SnCl)_2(\mu_3\text{-}CO_3)(Ph_3Sn)(Hbpa)]\cdot H_2O$ (**1**), and a coordination polymer $^{1}_{\infty}[(Ph_3SnCl)(Ph_3Sn)_2(\mu_3\text{-}CO_3)(bpa)]\cdot H_2O$ (**2**), respectively. X-Ray crystal structure analysis reveals that both compounds contain a rare trinuclear carbonato-centered core $C(OSnPh_3)_3$. The supramolecular architecture of compound **1**, assembled by hydrogen-bond interactions, is described.

The capture of atmospheric carbon dioxide, a major greenhouse gas, is of great current interest; therefore, various methods to reduce the CO_2 levels have been investigated in recent years [1]. Most of these methods are based upon physical adsorption into porous materials (Metal-Organic Frameworks, MOFs) [2], and on chemical reactions with basic reagents [3].

Reactions of carbon dioxide with organotin compounds have been previously reported. The CO_2 insertion into Sn—O bonds is facile in the alkoxide series and compounds exhibiting a $C(OSnR_3)_3$ core with $R = CH_3$, ${}^{i}C_4H_9$, ${}^{n}C_4H_9$, as well as some polymeric organotin carbonates are known [4].

We report here an unexpected capture of atmospheric carbon dioxide which occurred during the reaction of triphenyltin chloride (Ph_3SnCl) with 1,2-bis(4-pyridyl)ethane (bpa), in methanol and aqueous ammonia, an alkaline environment that favors the capture of CO_2. The reaction was studied with the aim of obtaining coordination polymers or supramolecular architectures with organometallic nodes linked through diamine spacers [5]. Two different compounds were obtained just by using different reaction temperatures. Thus, at 4 °C, a trinuclear complex, $[(Ph_3SnCl)_2(\mu_3\text{-}CO_3)(Ph_3Sn)(Hbpa)]\cdot H_2O$ (**1**) [6], was isolated, whereas at room temperature (ca 25 °C) a 1-D coordination polymer, $^{1}_{\infty}[(Ph_3SnCl)(Ph_3Sn)_2(\mu_3\text{-}CO_3)(bpa)]\cdot H_2O$ (**2**), was obtained [7].

Both compounds were investigated by single crystal X-ray diffraction [8] and were found to contain a trinuclear unit, $C(OSnPh_3)_3$, built around the carbonato anion. To the best of our knowledge, the only similar case is the formation of $[(Ph_3Sn)_3(CO_3)(EtOH)_3]\cdot Cl\cdot(ntb)\ H_2O$, where ntb = tris(2-benzimidazolyl-methyl)amine, obtained from Ph_3SnCl, NaOEt and ntb in open atmosphere. In this compound the trinuclear units formed around the CO_3 group are nodes connected into a 3D supramolecular network linked through OH¨N bonds [9].

Crystallographic analysis reveals that compound **1** crystallizes in the monoclinic centrosymmetric space group $P2_1/c$. The molecular structure of compound **1** is shown in Fig. 1. The central CO_3 group coordinates

Fig. 1. The molec
with partial num
protonates N2 is

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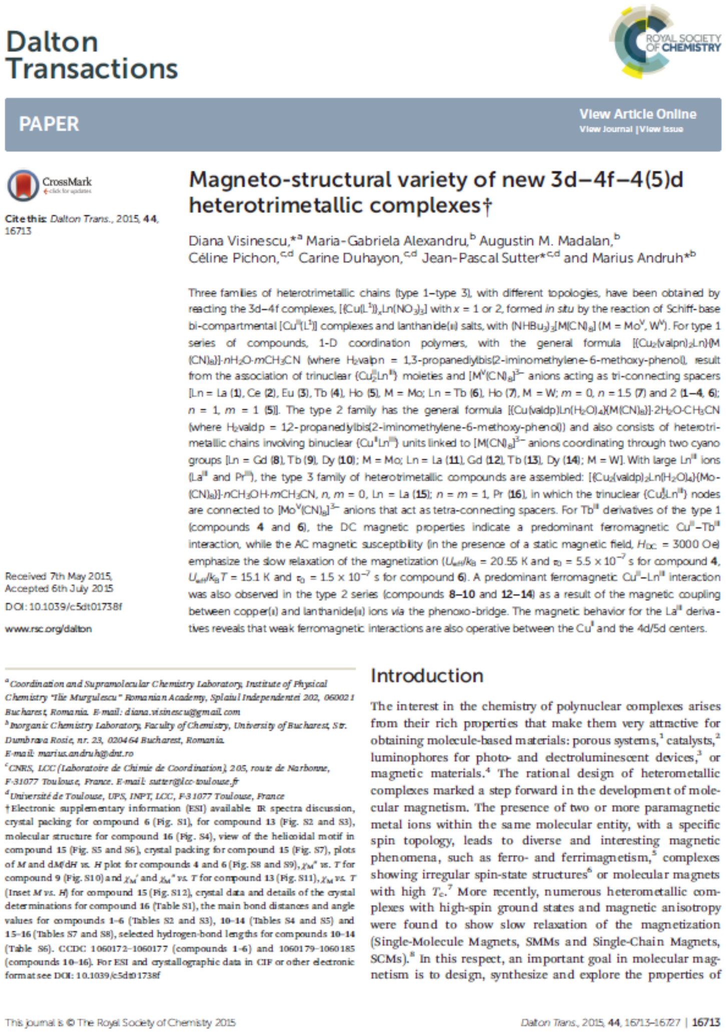
Dissemination of Results 2015

14. D. Visinescu, M.G. Alexandru, A.M. Madalan, C. Pichon, C. Duhayon, J.P. Sutter, M. Andruh, *Magneto-structural variety of new 3d–4f–4(5)d heterotrimetallic complexes*, Dalton Trans., **2015**, *44*, 16713-16727.



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PAPER

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Magneto-structural variety of new 3d–4f–4(5)d heterotrimetallic complexes†

Diana Visinescu,*[a] Maria-Gabriela Alexandru,[b] Augustin M. Madalan,[b] Céline Pichon,[c,d] Carine Duhayon,[c,d] Jean-Pascal Sutter*[c,d] and Marius Andruh*[b]

Three families of heterotrimetallic chains (type 1–type 3), with different topologies, have been obtained by reacting the 3d–4f complexes, $[\{Cu(L^1)\}_xLn(NO_3)_3]$ with $x = 1$ or 2, formed *in situ* by the reaction of Schiff-base bi-compartmental $[Cu^{II}(L^1)]$ complexes and lanthanide(III) salts, with $(NHBu_3)_3[M(CN)_8]$ ($M = Mo^V, W^V$). For type 1 series of compounds, 1-D coordination polymers, with the general formula $[\{Cu_2(valpn)_2Ln\}\{M(CN)_8\}]\cdot nH_2O\cdot mCH_3CN$ (where H_2valpn = 1,3-propanediylbis(2-iminomethylene-6-methoxy-phenol)), result from the association of trinuclear $\{Cu^{II}_2Ln^{III}\}$ moieties and $[M^V(CN)_8]^{3-}$ anions acting as tri-connecting spacers [Ln = La (**1**), Ce (**2**), Eu (**3**), Tb (**4**), Ho (**5**), M = Mo; Ln = Tb (**6**), Ho (**7**), M = W; $m = 0$, $n = 1.5$ (**7**) and 2 (**1–4**, **6**); $n = 1$, $m = 1$ (**5**)]. The type 2 family has the general formula $[\{Cu(valdp)Ln(H_2O)_4\}\{M(CN)_8\}]\cdot 2H_2O\cdot CH_3CN$ (where H_2valdp = 1,2-propanediylbis(2-iminomethylene-6-methoxy-phenol)) and also consists of heterotrimetallic chains involving binuclear $\{Cu^{II}Ln^{III}\}$ units linked to $[M(CN)_8]^{3-}$ anions coordinating through two cyano groups [Ln = Gd (**8**), Tb (**9**), Dy (**10**); M = Mo; Ln = La (**11**), Gd (**12**), Tb (**13**), Dy (**14**); M = W]. With large Ln^{III} ions (La^{III} and Pr^{III}), the type 3 family of heterotrimetallic compounds are assembled: $[\{Cu_2(valdp)_2Ln(H_2O)_4\}\{Mo(CN)_8\}]\cdot nCH_3OH\cdot mCH_3CN$, $n, m = 0$, Ln = La (**15**); $n = m = 1$, Pr (**16**), in which the trinuclear $\{Cu^{II}_2Ln^{III}\}$ nodes are connected to $[Mo^V(CN)_8]^{3-}$ anions that act as tetra-connecting spacers. For Tb^{III} derivatives of the type 1 (compounds **4** and **6**), the DC magnetic properties indicate a predominant ferromagnetic Cu^{II}–Tb^{III} interaction, while the AC magnetic susceptibility (in the presence of a static magnetic field, H_{DC} = 3000 Oe) emphasize the slow relaxation of the magnetization (U_{eff}/k_B = 20.55 K and $\tau_0 = 5.5 \times 10^{-7}$ s for compound **4**, U_{eff}/k_BT = 15.1 K and $\tau_0 = 1.5 \times 10^{-7}$ s for compound **6**). A predominant ferromagnetic Cu^{II}–Ln^{III} interaction was also observed in the type 2 series (compounds **8–10** and **12–14**) as a result of the magnetic coupling between copper(II) and lanthanide(III) ions *via* the phenoxo-bridge. The magnetic behavior for the La^{III} derivatives reveals that weak ferromagnetic interactions are also operative between the Cu^{II} and the 4d/5d centers.

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Introduction

The interest in the chemistry of polynuclear complexes arises from their rich properties that make them very attractive for obtaining molecule-based materials: porous systems,[1] catalysts,[2] luminophores for photo- and electroluminescent devices,[3] or magnetic materials.[4] The rational design of heterometallic complexes marked a step forward in the development of molecular magnetism. The presence of two or more paramagnetic metal ions within the same molecular entity, with a specific spin topology, leads to diverse and interesting magnetic phenomena, such as ferro- and ferrimagnetism,[5] complexes showing irregular spin-state structures[6] or molecular magnets with high T_c.[7] More recently, numerous heterometallic complexes with high-spin ground states and magnetic anisotropy were found to show slow relaxation of the magnetization (Single-Molecule Magnets, SMMs and Single-Chain Magnets, SCMs).[8] In this respect, an important goal in molecular magnetism is to design, synthesize and explore the properties of

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† Electronic supplementary information (ESI) available: IR spectra discussion, crystal packing for compound **6** (Fig. S1), for compound **13** (Fig. S2 and S3), molecular structure for compound **16** (Fig. S4), view of the helicoidal motif in compound **15** (Fig. S5 and S6), crystal packing for compound **15** (Fig. S7), plots of M and dM/dH *vs.* H plot for compounds **4** and **6** (Fig. S8 and S9), χ_M'' *vs.* T for compound **9** (Fig. S10) and χ_M' and χ_M'' *vs.* T for compound **13** (Fig. S11), χ_M *vs.* T (Inset M *vs.* H) for compound **15** (Fig. S12), crystal data and details of the crystal determinations for compound **16** (Table S1), the main bond distances and angle values for compounds **1–6** (Tables S2 and S3), **10–14** (Tables S4 and S5) and **15–16** (Tables S7 and S8), selected hydrogen-bond lengths for compounds **10–14** (Table S6). CCDC 1060172–1060177 (compounds **1–6**) and 1060179–1060185 (compounds **10–16**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt01738f

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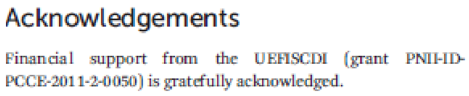
PAPER
Diana Visinescu, Jean-Pascal Sutter, Marius Andruh *et al.*
Magneto-structural variety of new 3d–4f–4(5)d heterotrimetallic complexes



Acknowledgements

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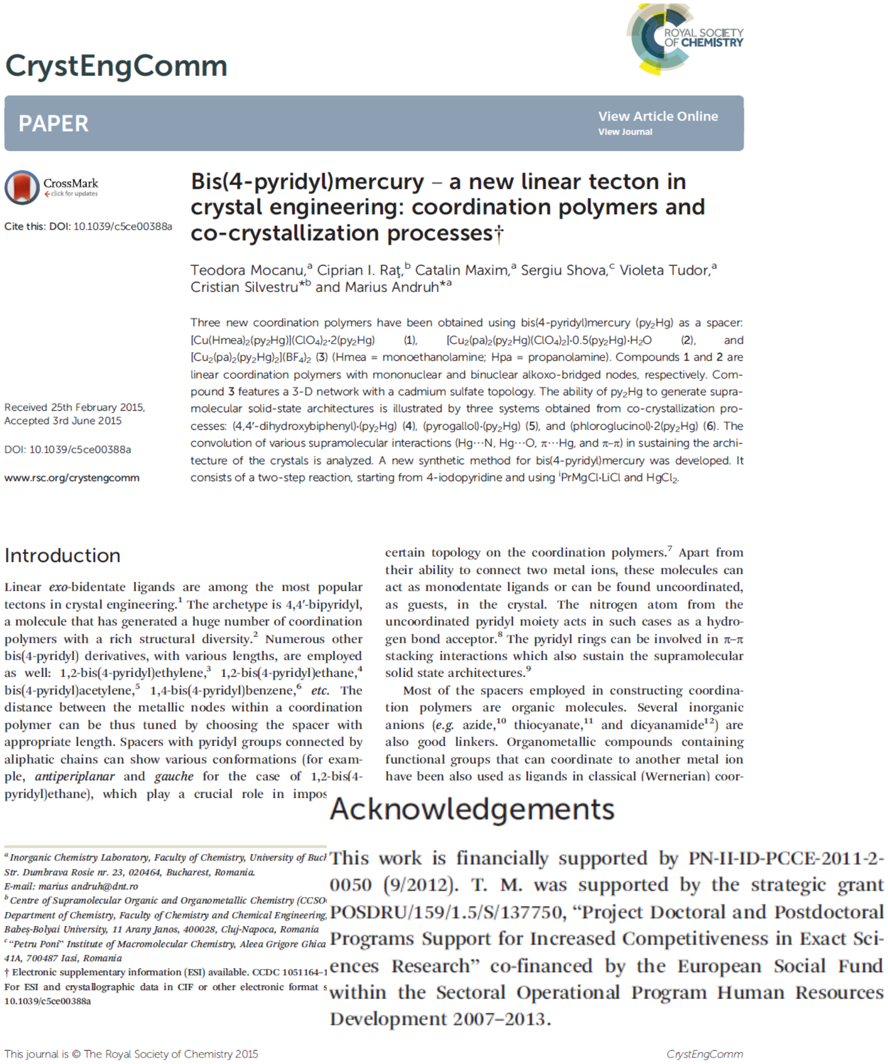
Dissemination of Results 2015

15. T. Mocanu, C.I. Rat, C. Maxim, S. Shova, V. Tudor, C. Silvestru, M. Andruh, *Bis(4-pyridyl)mercury – a new linear tecton in crystal engineering: coordination polymers and co-crystallization processes*, *CrystEngComm*, **2015**, *17*, 5474-5487.

16. M.G. Alexandru, D. Visinescu, M. Andruh, N. Marino, D. Armentano, J. Cano, F. Lloret, M. Julve, *Heterotrimetallic coordination polymers: {CuIILnIIIFeIII} chains and {NiIILnIIIFeIII} layers: Synthesis, crystal structures, and magnetic properties*, Chemistry A European Journal, **2015**, *21*, 5429-5446.



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Bis(4-pyridyl)mercury – a new linear tecton in crystal engineering: coordination polymers and co-crystallization processes†

Teodora Mocanu,[a] Ciprian I. Raţ,[b] Catalin Maxim,[a] Sergiu Shova,[c] Violeta Tudor,[a] Cristian Silvestru*[b] and Marius Andruh*[a]

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Three new coordination polymers have been obtained using bis(4-pyridyl)mercury (py_2Hg) as a spacer: $[Cu(Hmea)_2(py_2Hg)](ClO_4)_2 \cdot 2(py_2Hg)$ (**1**), $[Cu_2(pa)_2(py_2Hg)(ClO_4)_2] \cdot 0.5(py_2Hg) \cdot H_2O$ (**2**), and $[Cu_2(pa)_2(py_2Hg)_2](BF_4)_2$ (**3**) (Hmea = monoethanolamine; Hpa = propanolamine). Compounds **1** and **2** are linear coordination polymers with mononuclear and binuclear alkoxo-bridged nodes, respectively. Compound **3** features a 3-D network with a cadmium sulfate topology. The ability of py_2Hg to generate supramolecular solid-state architectures is illustrated by three systems obtained from co-crystallization processes: (4,4′-dihydroxybiphenyl)·(py_2Hg) (**4**), (pyrogallol)·(py_2Hg) (**5**), and (phloroglucinol)·2(py_2Hg) (**6**). The convolution of various supramolecular interactions (Hg···N, Hg···O, π···Hg, and π–π) in sustaining the architecture of the crystals is analyzed. A new synthetic method for bis(4-pyridyl)mercury was developed. It consists of a two-step reaction, starting from 4-iodopyridine and using $^{i}PrMgCl \cdot LiCl$ and $HgCl_2$.

Introduction

Linear *exo*-bidentate ligands are among the most popular tectons in crystal engineering.[1] The archetype is 4,4′-bipyridyl, a molecule that has generated a huge number of coordination polymers with a rich structural diversity.[2] Numerous other bis(4-pyridyl) derivatives, with various lengths, are employed as well: 1,2-bis(4-pyridyl)ethylene,[3] 1,2-bis(4-pyridyl)ethane,[4] bis(4-pyridyl)acetylene,[5] 1,4-bis(4-pyridyl)benzene,[6] *etc.* The distance between the metallic nodes within a coordination polymer can be thus tuned by choosing the spacer with appropriate length. Spacers with pyridyl groups connected by aliphatic chains can show various conformations (for example, *antiperiplanar* and *gauche* for the case of 1,2-bis(4-pyridyl)ethane), which play a crucial role in impos

certain topology on the coordination polymers.[7] Apart from their ability to connect two metal ions, these molecules can act as monodentate ligands or can be found uncoordinated, as guests, in the crystal. The nitrogen atom from the uncoordinated pyridyl moiety acts in such cases as a hydrogen bond acceptor.[8] The pyridyl rings can be involved in π–π stacking interactions which also sustain the supramolecular solid state architectures.[9]

Most of the spacers employed in constructing coordination polymers are organic molecules. Several inorganic anions (*e.g.* azide,[10] thiocyanate,[11] and dicyanamide[12]) are also good linkers. Organometallic compounds containing functional groups that can coordinate to another metal ion have been also used as ligands in classical (Wernerian) coor-

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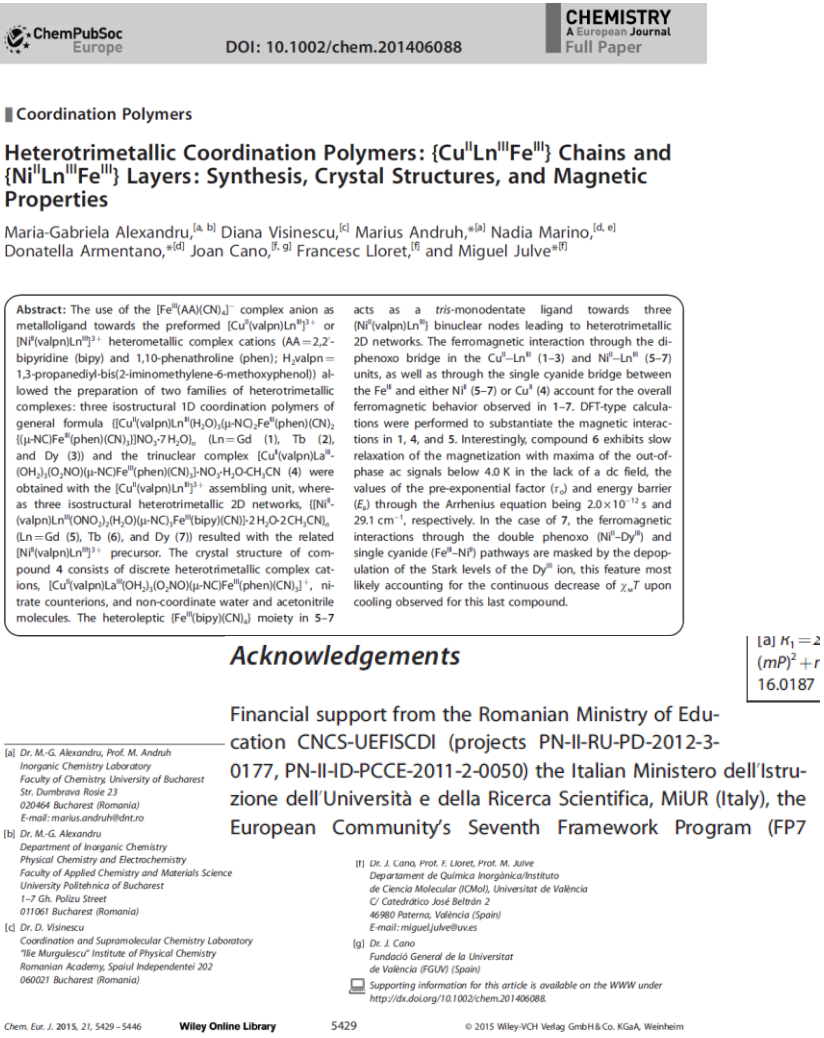
† Electronic supplementary information (ESI) available. CCDC 1051164–1 For ESI and crystallographic data in CIF or other electronic format s 10.1039/c5ce00388a



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Coordination Polymers

Heterotrimetallic Coordination Polymers: $\{Cu^{II}Ln^{III}Fe^{III}\}$ Chains and $\{Ni^{II}Ln^{III}Fe^{III}\}$ Layers: Synthesis, Crystal Structures, and Magnetic Properties

Maria-Gabriela Alexandru,[a, b] Diana Visinescu,[c] Marius Andruh,*[a] Nadia Marino,[d, e] Donatella Armentano,*[d] Joan Cano,[f, g] Francesc Lloret,[f] and Miguel Julve*[f]

Abstract: The use of the $[Fe^{III}(AA)(CN)_4]^-$ complex anion as metalloligand towards the preformed $[Cu^{II}(valpn)Ln^{III}]^{3+}$ or $[Ni^{II}(valpn)Ln^{III}]^{3+}$ heterometallic complex cations (AA = 2,2′-bipyridine (bipy) and 1,10-phenathroline (phen); H_2valpn = 1,3-propanediyl-bis(2-iminomethylene-6-methoxyphenol)) allowed the preparation of two families of heterotrimetallic complexes: three isostructural 1D coordination polymers of general formula $\{[Cu^{II}(valpn)Ln^{III}(H_2O)_3(\mu\text{-}NC)_2Fe^{III}(phen)(CN)_2\{(\mu\text{-}NC)Fe^{III}(phen)(CN)_3\}]NO_3 \cdot 7H_2O\}_n$ (Ln = Gd (**1**), Tb (**2**), and Dy (**3**)) and the trinuclear complex $[Cu^{II}(valpn)La^{III}(OH_2)_3(O_2NO)(\mu\text{-}NC)Fe^{III}(phen)(CN)_3] \cdot NO_3 \cdot H_2O \cdot CH_3CN$ (**4**) were obtained with the $[Cu^{II}(valpn)Ln^{III}]^{3+}$ assembling unit, whereas three isostructural heterotrimetallic 2D networks, $\{[Ni^{II}(valpn)Ln^{III}(ONO_2)_2(H_2O)(\mu\text{-}NC)_3Fe^{III}(bipy)(CN)] \cdot 2H_2O \cdot 2CH_3CN\}_n$ (Ln = Gd (**5**), Tb (**6**), and Dy (**7**)) resulted with the related $[Ni^{II}(valpn)Ln^{III}]^{3+}$ precursor. The crystal structure of compound **4** consists of discrete heterotrimetallic complex cations, $[Cu^{II}(valpn)La^{III}(OH_2)_3(O_2NO)(\mu\text{-}NC)Fe^{III}(phen)(CN)_3]^+$, nitrate counterions, and non-coordinate water and acetonitrile molecules. The heteroleptic $\{Fe^{III}(bipy)(CN)_4\}$ moiety in **5–7** acts as a *tris*-monodentate ligand towards three $\{Ni^{II}(valpn)Ln^{III}\}$ binuclear nodes leading to heterotrimetallic 2D networks. The ferromagnetic interaction through the diphenoxo bridge in the Cu^{II}–Ln^{III} (**1–3**) and Ni^{II}–Ln^{III} (**5–7**) units, as well as through the single cyanide bridge between the Fe^{III} and either Ni^{II} (**5–7**) or Cu^{II} (**4**) account for the overall ferromagnetic behavior observed in **1–7**. DFT-type calculations were performed to substantiate the magnetic interactions in **1**, **4**, and **5**. Interestingly, compound **6** exhibits slow relaxation of the magnetization with maxima of the out-of-phase ac signals below 4.0 K in the lack of a dc field, the values of the pre-exponential factor (τ_o) and energy barrier (E_a) through the Arrhenius equation being 2.0×10^{-12} s and 29.1 cm^{-1}, respectively. In the case of **7**, the ferromagnetic interactions through the double phenoxo (Ni^{II}–Dy^{III}) and single cyanide (Fe^{III}–Ni^{II}) pathways are masked by the depopulation of the Stark levels of the Dy^{III} ion, this feature most likely accounting for the continuous decrease of $\chi_M T$ upon cooling observed for this last compound.

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[a] $R_1 = 2$
$(mP)^2 + r$
16.0187

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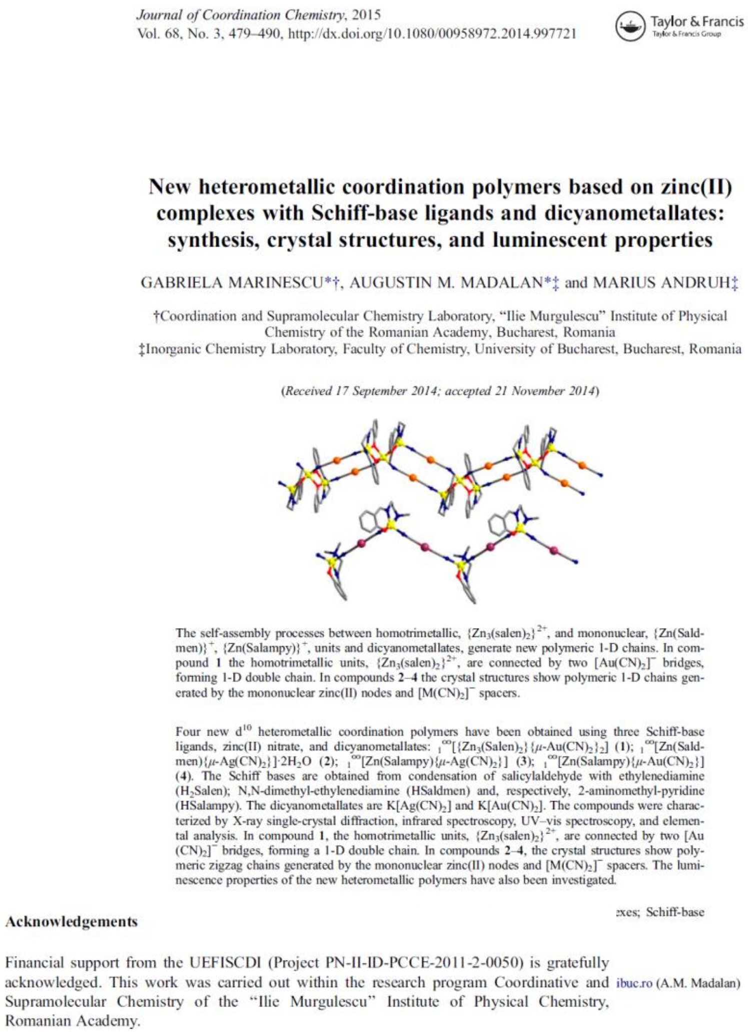
Dissemination of Results 2015

17. G. Marinescu, A.M. Madalan, M. Andruh, *New heterometallic coordination polymers based on zinc(II) complexes with Schiff-base ligands and cicyanometallates:synthesis, crystal structures, and luminescent properties*, *Journal of Coordination Chemistry*, **2015**, *68*, 479-490.

18. C. Paraschiv, A. Cucos, S. Shova, A.M. Madalan, C. Maxim, D. Visinescu, B. Cojocaru, V.I. Parvulescu, M. Andruh, *New Zn(II) coordination polymers constructed from amino-alcohols and aromatic dicarboxylic acids: Synthesis, structure, photocatalytic properties, and solid-state conversion to ZnO*, Crystal Growth & Design, **2015**, *15*, 799-811.



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New heterometallic coordination polymers based on zinc(II) complexes with Schiff-base ligands and dicyanometallates: synthesis, crystal structures, and luminescent properties

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The self-assembly processes between homotrimetallic, $\{Zn_3(salen)_2\}^{2+}$, and mononuclear, $\{Zn(Saldmen)\}^+$, $\{Zn(Salampy)\}^+$, units and dicyanometallates, generate new polymeric 1-D chains. In compound **1** the homotrimetallic units, $\{Zn_3(salen)_2\}^{2+}$, are connected by two $[Au(CN)_2]^-$ bridges, forming 1-D double chain. In compounds **2**–**4** the crystal structures show polymeric 1-D chains generated by the mononuclear zinc(II) nodes and $[M(CN)_2]^-$ spacers.

Four new d^{10} heterometallic coordination polymers have been obtained using three Schiff-base ligands, zinc(II) nitrate, and dicyanometallates: ${}_1^{\infty}[\{Zn_3(Salen)_2\}\{\mu\text{-}Au(CN)_2\}_2]$ (**1**); ${}_1^{\infty}[Zn(Saldmen)\{\mu\text{-}Ag(CN)_2\}]\cdot 2H_2O$ (**2**); ${}_1^{\infty}[Zn(Salampy)\{\mu\text{-}Ag(CN)_2\}]$ (**3**); ${}_1^{\infty}[Zn(Salampy)\{\mu\text{-}Au(CN)_2\}]$ (**4**). The Schiff bases are obtained from condensation of salicylaldehyde with ethylenediamine (H_2Salen); N,N-dimethyl-ethylenediamine (HSaldmen) and, respectively, 2-aminomethyl-pyridine (HSalampy). The dicyanometallates are $K[Ag(CN)_2]$ and $K[Au(CN)_2]$. The compounds were characterized by X-ray single-crystal diffraction, infrared spectroscopy, UV–vis spectroscopy, and elemental analysis. In compound **1**, the homotrimetallic units, $\{Zn_3(salen)_2\}^{2+}$, are connected by two $[Au(CN)_2]^-$ bridges, forming a 1-D double chain. In compounds **2**–**4**, the crystal structures show polymeric zigzag chains generated by the mononuclear zinc(II) nodes and $[M(CN)_2]^-$ spacers. The luminescence properties of the new heterometallic polymers have also been investigated.

xes; Schiff-base

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New Zn(II) Coordination Polymers Constructed from Amino-Alcohols and Aromatic Dicarboxylic Acids: Synthesis, Structure, Photocatalytic Properties, and Solid-State Conversion to ZnO

Carmen Paraschiv,*[†] Andrei Cucos,[†] Sergiu Shova,[‡] Augustin M. Madalan,[§] Catalin Maxim,[§] Diana Visinescu,[∥] Bogdan Cojocaru,[⊥] Vasile I. Parvulescu,*[⊥] and Marius Andruh*[§]

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Ⓢ *Supporting Information*

ABSTRACT: Four new coordination polymers have been obtained solvothermally from the reactions of $Zn(NO_3)_2\cdot 6H_2O$ with 1,2-, 1,3-, or 1,4-benzedicarboxylic acids in the presence of various amino-alcohols: ${}_1^{\infty}[Zn_2(Htea)_2(1,2\text{-}bdc)]$ (**1**), ${}_1^{\infty}[Zn(H_3tris)(1,3\text{-}bdc)(CH_3OH)]$ (**2**), ${}_3^{\infty}[Zn_5(Htea)_2(1,3\text{-}bdc)_3(H_2O)]\cdot 2.6H_2O$ (**3**), and ${}_3^{\infty}[Zn_3(H_2dea)_2(1,4\text{-}bdc)_3]$ (**4**) (H_3tea = triethanolamine, H_3tris = tris(hydroxymethyl)aminomethane, H_2dea = diethanolamine, 1,2-H_2bdc =1,2-benzenedicarboxylic acid, 1,3-H_2bdc =1,3-benzenedicarboxylic acid, and 1,4-H_2bdc =1,4-benzenedicarboxylic acid). Their crystal structures, thermogravimetric analyses, solid-state transformation to ZnO and characterization of the resultant zinc oxide particles are reported. Compounds **1** and **2** show three-dimensional (3D) supramolecular architectures, generated from the interconnection of the zigzag (in **1**) and respectively the linear (in **2**) chains through hydrogen bonding interactions. The crystal structure of **3** revealed the presence of five different types of zinc atoms that are successively linked through carboxilato or alkoxo bridges in a helicoidal chain running along the crystallographic *a* axis. Both right-handed (*P*) and left-handed (*M*) helices are present in the crystal, and they are alternately interconnected by pairs of isophthalato bridges, resulting in channels of hexagonal shape, filled with water molecules. Compound **4** has a 3D structure in which linear centrosymmetric $\{Zn_3(H_2dea)_2\}^{6+}$ nodes are joined by terephthalate bridges. Owing to its porous network, compound **3** was tested in two selective reactions: photooxidation of phenol to hydroquinone and aerobic photooxidative condensation of benzylamine to *N*-benzylidenebenzylamine.

■ INTRODUCTION

The chemistry of multifunctional coordination polymers (CPs) has rapidly become one of the most challenging and appealing research areas due to their potential in both traditional and emerging applications: gas storage,[1−8] separation,[9−15] catalysis,[16−23] luminescence,[24−30] recognition,[31−33] bioactive molecules,[34−37] and magnetism.[38−45] A rich variety of structures and topologies have been rationally designed and synthesized by judicious selection of connectors (metal ions or metal clusters) and linkers (organic molecules, inorganic anions, or metalloligands).[46−50] The sum of the distinctive characteristics of the inorganic and organic components and their possible synergistic action could provide novel and intriguing properties for the resulting materials. Furthermore, the final architecture can be influenced by auxiliary ligands, solvent molecules, temperature, pH, and coordinated or uncoordinated anions.

Numerous multitopic ligands with two or more discrete metal-binding sites have been used in the construction of coordination polymers. Conventional linkers are usually organic compounds containing donor atoms or groups of donor atoms (polycarboxylates,[51−59] phenolates,[60−62] amines,[63−67] pyridyl derivatives,[68−80] sulfonates,[81−87] phosphonates,[88,89] and azolates[90−93]). In particular, carboxylate-based systems, especially three-dimensional (3D) porous metal organic frameworks (MOFs) constructed with rigid aromatic backbones (benzene-, naphthalene-, anthracene-, and pyrene-based derivatives), have attracted considerable attention due to the tunability of their structures and properties and their suitability for hydrogen storage, sorption, separation, and sensing.[94−102]

The node-and-spacer approach[103,104] proved to be a

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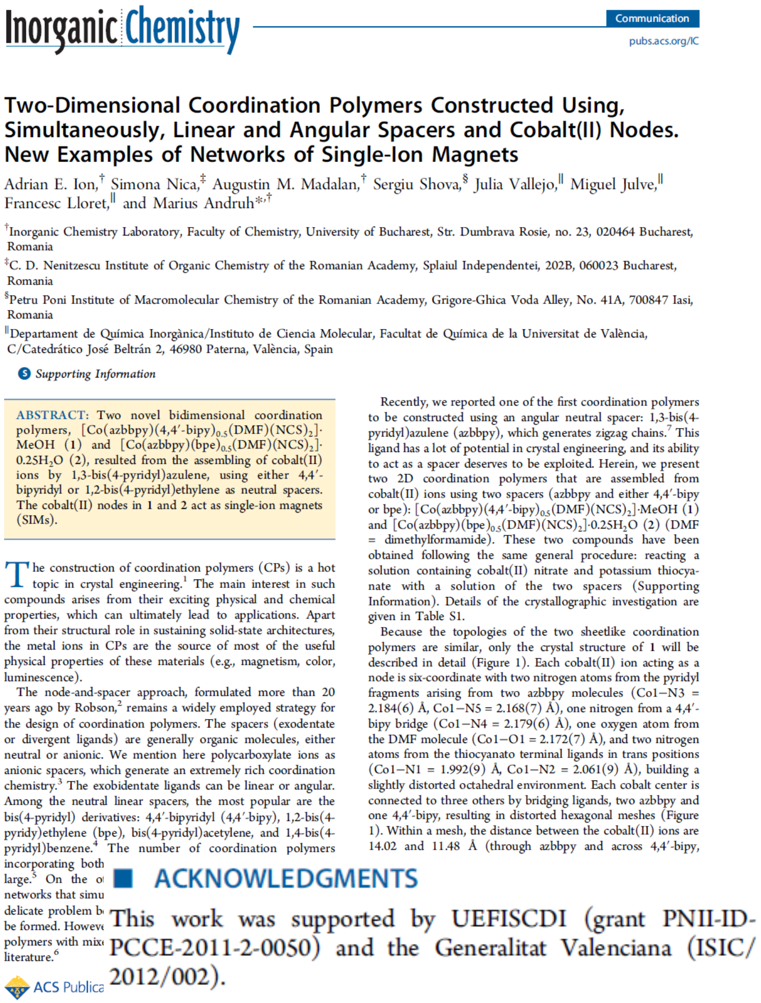
19. A.E. Ion, S. Nica, A.M. Madalan, S. Shova, J. Vallejo, M. Julve, F. Lloret, M. Andruh, *Two-dimensional coordination polymers constructed using, simultaneously, linear and angular spacers and cobalt(II) nodes. New examples of networks of single-ion magnets*, *Inorg. Chem.*, **2015**, *54*, 16-18.

20. A.S. Dinca, C. Maxim, B. Cojocaru, F. Lloret, M. Julve, M. Andruh, *A two-dimensional coordination polymer constructed from binuclear copper(II) metalloligands and manganese(II) ions: Synthesis, crystal structure and magnetic properties*, Inorganica Chimica Acta, **2016**, *440*, 148-153.



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Two-Dimensional Coordination Polymers Constructed Using, Simultaneously, Linear and Angular Spacers and Cobalt(II) Nodes. New Examples of Networks of Single-Ion Magnets

Adrian E. Ion,[†] Simona Nica,[‡] Augustin M. Madalan,[†] Sergiu Shova,[§] Julia Vallejo,[‖] Miguel Julve,[‖] Francesc Lloret,[‖] and Marius Andruh*[,†]

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Supporting Information

ABSTRACT: Two novel bidimensional coordination polymers, $[Co(azbbpy)(4,4'\text{-}bipy)_{0.5}(DMF)(NCS)_2]\cdot MeOH$ (**1**) and $[Co(azbbpy)(bpe)_{0.5}(DMF)(NCS)_2]\cdot 0.25H_2O$ (**2**), resulted from the assembling of cobalt(II) ions by 1,3-bis(4-pyridyl)azulene, using either 4,4′-bipyridyl or 1,2-bis(4-pyridyl)ethylene as neutral spacers. The cobalt(II) nodes in **1** and **2** act as single-ion magnets (SIMs).

The construction of coordination polymers (CPs) is a hot topic in crystal engineering.[1] The main interest in such compounds arises from their exciting physical and chemical properties, which can ultimately lead to applications. Apart from their structural role in sustaining solid-state architectures, the metal ions in CPs are the source of most of the useful physical properties of these materials (e.g., magnetism, color, luminescence).

The node-and-spacer approach, formulated more than 20 years ago by Robson,[2] remains a widely employed strategy for the design of coordination polymers. The spacers (exodentate or divergent ligands) are generally organic molecules, either neutral or anionic. We mention here polycarboxylate ions as anionic spacers, which generate an extremely rich coordination chemistry.[3] The exobidentate ligands can be linear or angular. Among the neutral linear spacers, the most popular are the bis(4-pyridyl) derivatives: 4,4′-bipyridyl (4,4′-bipy), 1,2-bis(4-pyridy)ethylene (bpe), bis(4-pyridyl)acetylene, and 1,4-bis(4-pyridyl)benzene.[4] The number of coordination polymers
incorporating both
large.[5] On the o
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be formed. Howeve
polymers with mix
literature.[6]

ACS Publica

Recently, we reported one of the first coordination polymers to be constructed using an angular neutral spacer: 1,3-bis(4-pyridyl)azulene (azbbpy), which generates zigzag chains.[7] This ligand has a lot of potential in crystal engineering, and its ability to act as a spacer deserves to be exploited. Herein, we present two 2D coordination polymers that are assembled from cobalt(II) ions using two spacers (azbbpy and either 4,4′-bipy or bpe): $[Co(azbbpy)(4,4'\text{-}bipy)_{0.5}(DMF)(NCS)_2]\cdot MeOH$ (**1**) and $[Co(azbbpy)(bpe)_{0.5}(DMF)(NCS)_2]\cdot 0.25H_2O$ (**2**) (DMF = dimethylformamide). These two compounds have been obtained following the same general procedure: reacting a solution containing cobalt(II) nitrate and potassium thiocyanate with a solution of the two spacers (Supporting Information). Details of the crystallographic investigation are given in Table S1.

Because the topologies of the two sheetlike coordination polymers are similar, only the crystal structure of **1** will be described in detail (Figure 1). Each cobalt(II) ion acting as a node is six-coordinate with two nitrogen atoms from the pyridyl fragments arising from two azbbpy molecules (Co1−N3 = 2.184(6) Å, Co1−N5 = 2.168(7) Å), one nitrogen from a 4,4′-bipy bridge (Co1−N4 = 2.179(6) Å), one oxygen atom from the DMF molecule (Co1−O1 = 2.172(7) Å), and two nitrogen atoms from the thiocyanato terminal ligands in trans positions (Co1−N1 = 1.992(9) Å, Co1−N2 = 2.061(9) Å), building a slightly distorted octahedral environment. Each cobalt center is connected to three others by bridging ligands, two azbbpy and one 4,4′-bipy, resulting in distorted hexagonal meshes (Figure 1). Within a mesh, the distance between the cobalt(II) ions are 14.02 and 11.48 Å (through azbbpy and across 4,4′-bipy,

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A two-dimensional coordination polymer constructed from binuclear copper(II) metalloligands and manganese(II) ions: Synthesis, crystal structure and magnetic properties

CrossMark

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ABSTRACT

The self-assembly process between the binuclear $[Cu_2(HL)(L)]^-$ complex and the manganese(II) ion affords a two-dimensional coordination polymer of formula $[Mn\{Cu_2(HL)(L)\}_2(H_2O)_2]_n$ (**1**) (H_3L = 3-hydroxyiminomethylsalicylic acid) where parallel ladder-like motifs of defective double cubanes of bis(phenoxo)dicopper(II) units as rods and *anti-syn* carboxylato bridges as rungs act as ligands towards tetraaqua-manganese(II) entities through the deprotonated oxime groups. The topology of **1** is compared with the one of another compound, $[Mn\{Cu_2(HL)(L)\}_2(H_2O)_4]\cdot 4H_2O\cdot 2DMF$ (**1′**) which was obtained in different conditions by Okawa et al. (J. Chem. Soc., Dalton Trans. (2001) 3119). Magnetic susceptibility measurements of **1** in the temperature range 2.0–300 K are practically determined by the occurrence of a very large antiferromagnetic coupling between the two copper(II) ions through the double phenoxido bridge [$J = -765(5)\ \text{cm}^{-1}$, the spin Hamiltonian being defined as $\mathbf{H} = -J\mathbf{S}_{Cu1}\cdot\mathbf{S}_{Cu2}$], a value which is as expected in the light of a recent magneto-structural correlation for bis(phenoxido)dicopper(II) complexes.

1. Introduction

3-Formylsalicylic acid is a valuable starting material for the synthesis of a rich variety of ligands [1]. Among these, the Schiff bases resulted from its condensation reactions with primary diamines are particularly useful as bicompartmental ligands (Scheme 1, **A**). Since the two sets of donor atoms are different (N_2O_2 and $O_2O'_2$), they favor the formation of heterobinuclear complexes, which have played an important role in the history
molecular magnetism. Indeed, one of the most important too
operating in the molecular magnetism field, namely the stri
orthogonality of the magnetic orbitals, which leads to ferroma
netic interactions, was illustrated by rationally designed Cu^{II}–V^{IV}
Cu^{II}–Cr^{III}, Ni^{II}–Cr^{III} complexes with side-off compartmental ligan
(**A**) [2]. If diamines with one primary and one tertiary am
groups are used for the condensation reactions, unsymmet
tetradentate ligands are formed (Scheme 1, **B**) [3]. Apart
Schiff bases, 3-formylsalicylic acid can generate other u
ligands. For example, the reaction with hydroxylamine af
the oxime derivative, H_3L (Scheme 1C), a proligand with mul
coordination sites. Its binuclear homometallic complexes

reported by Okawa et al. [4], who observed two configurations of the resulting species, with *cis*- and *trans*-arrangements of the ligands around the two metal centers (Scheme 2): $[M_2(HL)_2]$, $[M_2(HL)(L)]^-$, and $[M_2(L)_2]^{2-}$. For the second complex (*cis* configuration), the two organic molecules are assembled into what we can call a "supramolecular compartmental ligand", whose assembling is supported by the well-known hydrogen bond established between the protonated and deprotonated oxime groups [5]. The

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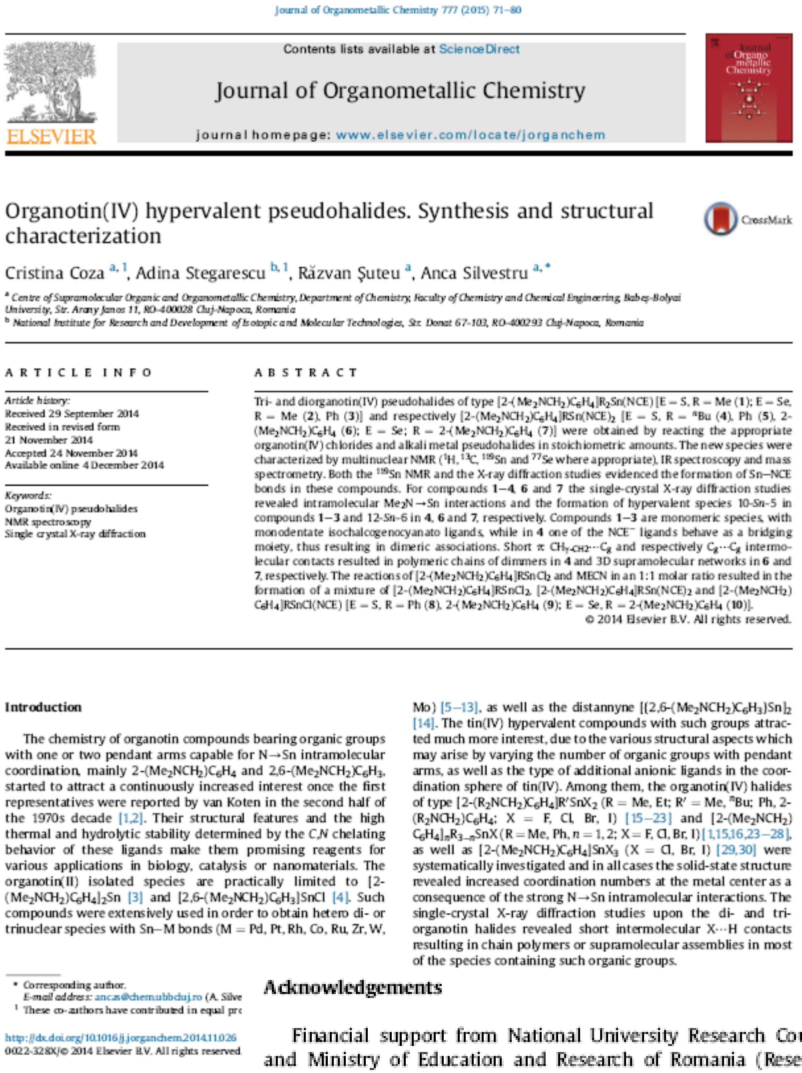
Dissemination of Results 2015

21. C. Coza, A. Stegarescu, R. Suteu, A. Silvestru, *Organotin(IV) hypervalent pseudohalides. Synthesis and structural characterization*, *Journal of Organometallic Chemistry,* **2015**, *777*, 71-80.

22. L. Pop, F. Dumitru, N.D. Hădade, Y.M. Legrand, A. van der Lee, M. Barboiu, I. Grosu, *Exclusive Hydrophobic Self-Assembly of Adaptive Solid-State Networks of Octasubstituted 9,9'-Spirobifluorenes*, *Org. Lett*. **2015**, *17*, 3494−3497.



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Organotin(IV) hypervalent pseudohalides. Synthesis and structural characterization

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ABSTRACT

Tri- and diorganotin(IV) pseudohalides of type $[2\text{-}(Me_2NCH_2)C_6H_4]R_2Sn(NCE)$ [E = S, R = Me (**1**); E = Se, R = Me (**2**), Ph (**3**)] and respectively $[2\text{-}(Me_2NCH_2)C_6H_4]RSn(NCE)_2$ [E = S, R = ^{n}Bu (**4**), Ph (**5**), $2\text{-}(Me_2NCH_2)C_6H_4$ (**6**); E = Se; R = $2\text{-}(Me_2NCH_2)C_6H_4$ (**7**)] were obtained by reacting the appropriate organotin(IV) chlorides and alkali metal pseudohalides in stoichiometric amounts. The new species were characterized by multinuclear NMR (^{1}H, ^{13}C, ^{119}Sn and ^{77}Se where appropriate), IR spectroscopy and mass spectrometry. Both the ^{119}Sn NMR and the X-ray diffraction studies evidenced the formation of Sn–NCE bonds in these compounds. For compounds **1–4**, **6** and **7** the single-crystal X-ray diffraction studies revealed intramolecular $Me_2N \rightarrow Sn$ interactions and the formation of hypervalent species 10-*Sn*-5 in compounds **1–3** and 12-*Sn*-6 in **4**, **6** and **7**, respectively. Compounds **1–3** are monomeric species, with monodentate isochalcogenocyanato ligands, while in **4** one of the NCE^- ligands behave as a bridging moiety, thus resulting in dimeric associations. Short π $CH_{\gamma\text{-}CH2}\cdots C_g$ and respectively $C_g\cdots C_g$ intermolecular contacts resulted in polymeric chains of dimmers in **4** and 3D supramolecular networks in **6** and **7**, respectively. The reactions of $[2\text{-}(Me_2NCH_2)C_6H_4]RSnCl_2$ and MECN in an 1:1 molar ratio resulted in the formation of a mixture of $[2\text{-}(Me_2NCH_2)C_6H_4]RSnCl_2$, $[2\text{-}(Me_2NCH_2)C_6H_4]RSn(NCE)_2$ and $[2\text{-}(Me_2NCH_2)C_6H_4]RSnCl(NCE)$ [E = S, R = Ph (**8**), $2\text{-}(Me_2NCH_2)C_6H_4$ (**9**); E = Se, R = $2\text{-}(Me_2NCH_2)C_6H_4$ (**10**)].

Introduction

The chemistry of organotin compounds bearing organic groups with one or two pendant arms capable for N→Sn intramolecular coordination, mainly $2\text{-}(Me_2NCH_2)C_6H_4$ and $2,6\text{-}(Me_2NCH_2)C_6H_3$, started to attract a continuously increased interest once the first representatives were reported by van Koten in the second half of the 1970s decade [1,2]. Their structural features and the high thermal and hydrolytic stability determined by the *C,N* chelating behavior of these ligands make them promising reagents for various applications in biology, catalysis or nanomaterials. The organotin(II) isolated species are practically limited to $[2\text{-}(Me_2NCH_2)C_6H_4]_2Sn$ [3] and $[2,6\text{-}(Me_2NCH_2)C_6H_3]SnCl$ [4]. Such compounds were extensively used in order to obtain hetero di- or trinuclear species with Sn–M bonds (M = Pd, Pt, Rh, Co, Ru, Zr, W, Mo) [5–13], as well as the distannyne $[\{2,6\text{-}(Me_2NCH_2)C_6H_3\}Sn]_2$ [14]. The tin(IV) hypervalent compounds with such groups attracted much more interest, due to the various structural aspects which may arise by varying the number of organic groups with pendant arms, as well as the type of additional anionic ligands in the coordination sphere of tin(IV). Among them, the organotin(IV) halides of type $[2\text{-}(R_2NCH_2)C_6H_4]R'SnX_2$ (R = Me, Et; R′ = Me, ^{n}Bu; Ph, $2\text{-}(R_2NCH_2)C_6H_4$; X = F, Cl, Br, I) [15–23] and $[2\text{-}(Me_2NCH_2)C_6H_4]_nR_{3-n}SnX$ (R = Me, Ph, *n* = 1, 2; X = F, Cl, Br, I) [1,15,16,23–28], as well as $[2\text{-}(Me_2NCH_2)C_6H_4]SnX_3$ (X = Cl, Br, I) [29,30] were systematically investigated and in all cases the solid-state structure revealed increased coordination numbers at the metal center as a consequence of the strong N→Sn intramolecular interactions. The single-crystal X-ray diffraction studies upon the di- and triorganotin halides revealed short intermolecular X···H contacts resulting in chain polymers or supramolecular assemblies in most of the species containing such organic groups.

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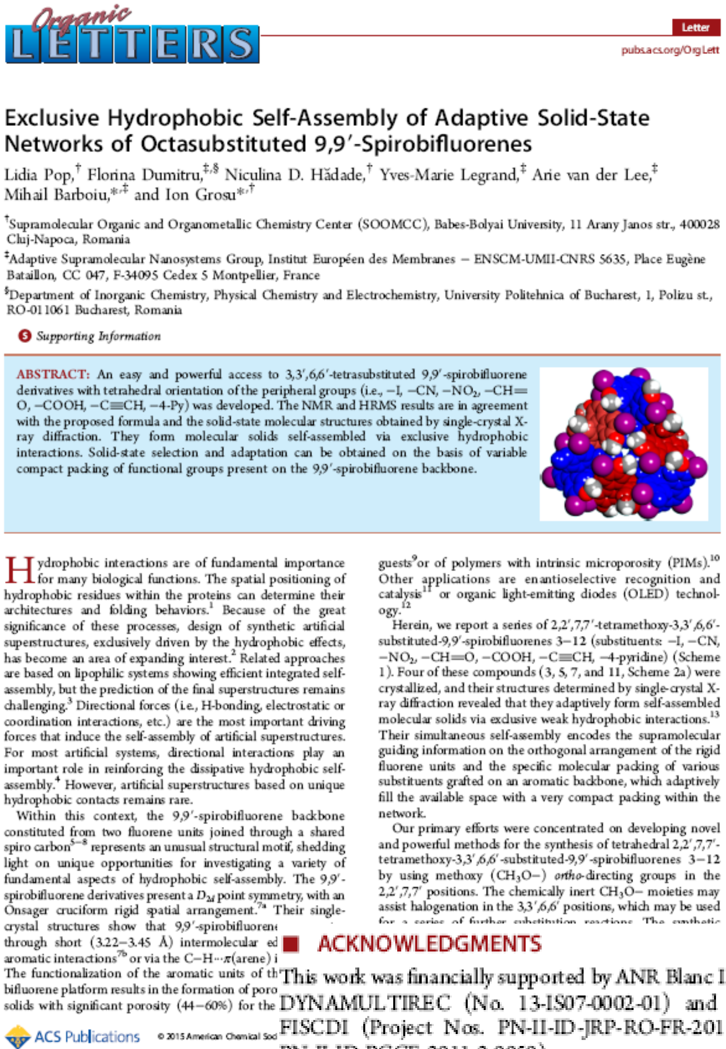

Organic LETTERS
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Exclusive Hydrophobic Self-Assembly of Adaptive Solid-State Networks of Octasubstituted 9,9′-Spirobifluorenes

Lidia Pop,[†] Florina Dumitru,[‡,§] Niculina D. Hădade,[†] Yves-Marie Legrand,[‡] Arie van der Lee,[‡] Mihail Barboiu,[*,‡] and Ion Grosu[*,†]

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Ⓢ *Supporting Information*

ABSTRACT: An easy and powerful access to 3,3′,6,6′-tetrasubstituted 9,9′-spirobifluorene derivatives with tetrahedral orientation of the peripheral groups (i.e., −I, −CN, $-NO_2$, −CH=O, −COOH, −C≡CH, −4-Py) was developed. The NMR and HRMS results are in agreement with the proposed formula and the solid-state molecular structures obtained by single-crystal X-ray diffraction. They form molecular solids self-assembled via exclusive hydrophobic interactions. Solid-state selection and adaptation can be obtained on the basis of variable compact packing of functional groups present on the 9,9′-spirobifluorene backbone.

Hydrophobic interactions are of fundamental importance for many biological functions. The spatial positioning of hydrophobic residues within the proteins can determine their architectures and folding behaviors.[1] Because of the great significance of these processes, design of synthetic artificial superstructures, exclusively driven by the hydrophobic effects, has become an area of expanding interest.[2] Related approaches are based on lipophilic systems showing efficient integrated self-assembly, but the prediction of the final superstructures remains challenging.[3] Directional forces (i.e., H-bonding, electrostatic or coordination interactions, etc.) are the most important driving forces that induce the self-assembly of artificial superstructures. For most artificial systems, directional interactions play an important role in reinforcing the dissipative hydrophobic self-assembly.[4] However, artificial superstructures based on unique hydrophobic contacts remains rare.

Within this context, the 9,9′-spirobifluorene backbone constituted from two fluorene units joined through a shared spiro carbon[5−8] represents an unusual structural motif, shedding light on unique opportunities for investigating a variety of fundamental aspects of hydrophobic self-assembly. The 9,9′-spirobifluorene derivatives present a D_{2d} point symmetry, with an Onsager cruciform rigid spatial arrangement.[7a] Their single-crystal structures show that 9,9′-spirobifluorene
through short (3.22−3.45 Å) intermolecular ed
aromatic interactions[7b] or via the C−H···π(arene) i
The functionalization of the aromatic units of th
bifluorene platform results in the formation of poro
solids with significant porosity (44−60%) for the

guests[9] or of polymers with intrinsic microporosity (PIMs).[10] Other applications are enantioselective recognition and catalysis[11] or organic light-emitting diodes (OLED) technology.[12]

Herein, we report a series of 2,2′,7,7′-tetramethoxy-3,3′,6,6′-substituted-9,9′-spirobifluorenes 3−12 (substituents: −I, −CN, $-NO_2$, −CH=O, −COOH, −C≡CH, −4-pyridine) (Scheme 1). Four of these compounds (3, 5, 7, and 11, Scheme 2a) were crystallized, and their structures determined by single-crystal X-ray diffraction revealed that they adaptively form self-assembled molecular solids via exclusive weak hydrophobic interactions.[13] Their simultaneous self-assembly encodes the supramolecular guiding information on the orthogonal arrangement of the rigid fluorene units and the specific molecular packing of various substituents grafted on an aromatic backbone, which adaptively fill the available space with a very compact packing within the network.

Our primary efforts were concentrated on developing novel and powerful methods for the synthesis of tetrahedral 2,2′,7,7′-tetramethoxy-3,3′,6,6′-substituted-9,9′-spirobifluorenes 3−12 by using methoxy (CH_3O-) *ortho*-directing groups in the 2,2′,7,7′ positions. The chemically inert CH_3O- moieties may assist halogenation in the 3,3′,6,6′ positions, which may be used for a series of further substitution reactions. The synthetic

ACS Publications

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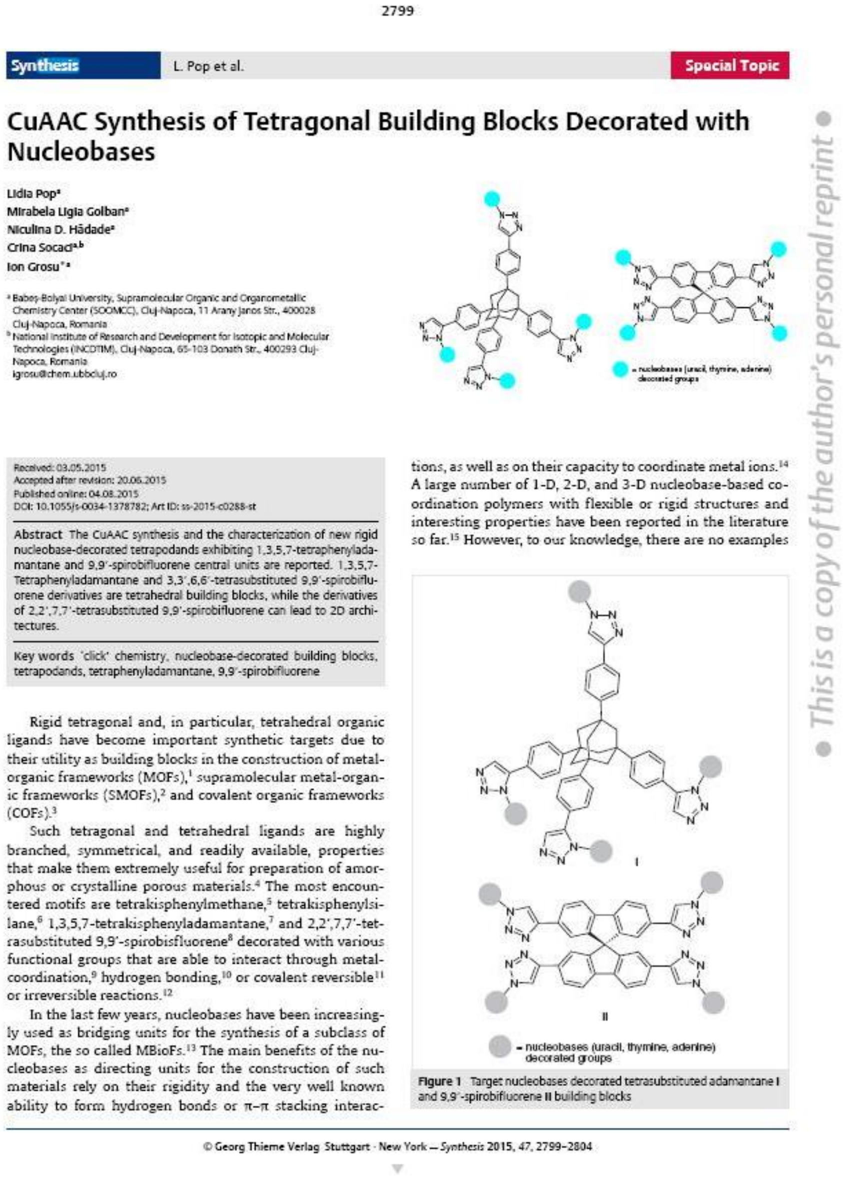
Dissemination of Results 2015

23. L. Pop, M.L. Golban, N.D. Hadade, C. Socaci, I. Grosu, *CuAAC Synthesis of Tetragonal Building Blocks Decorated with Nucleobases*, *SYNTHESIS-STUTTGART*, **2015**, *47*, 2799-2802.



CuAAC Synthesis of Tetragonal Building Blocks Decorated with Nucleobases

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● = nucleobases (uracil, thymine, adenine) decorated groups

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Abstract The CuAAC synthesis and the characterization of new rigid nucleobase-decorated tetrapodands exhibiting 1,3,5,7-tetraphenyladamantane and 9,9′-spirobifluorene central units are reported. 1,3,5,7-Tetraphenyladamantane and 3,3′,6,6′-tetrasubstituted 9,9′-spirobifluorene derivatives are tetrahedral building blocks, while the derivatives of 2,2′,7,7′-tetrasubstituted 9,9′-spirobifluorene can lead to 2D architectures.

Key words 'click' chemistry, nucleobase-decorated building blocks, tetrapodands, tetraphenyladamantane, 9,9′-spirobifluorene

Rigid tetragonal and, in particular, tetrahedral organic ligands have become important synthetic targets due to their utility as building blocks in the construction of metal-organic frameworks (MOFs),[1] supramolecular metal-organic frameworks (SMOFs),[2] and covalent organic frameworks (COFs).[3]

Such tetragonal and tetrahedral ligands are highly branched, symmetrical, and readily available, properties that make them extremely useful for preparation of amorphous or crystalline porous materials.[4] The most encountered motifs are tetrakisphenylmethane,[5] tetrakisphenylsilane,[6] 1,3,5,7-tetrakisphenyladamantane,[7] and 2,2′,7,7′-tetrasubstituted 9,9′-spirobisfluorene[8] decorated with various functional groups that are able to interact through metal-coordination,[9] hydrogen bonding,[10] or covalent reversible[11] or irreversible reactions.[12]

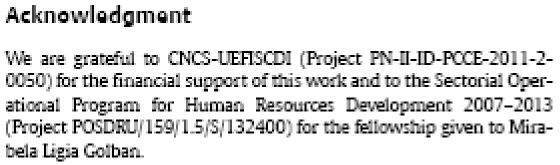
In the last few years, nucleobases have been increasingly used as bridging units for the synthesis of a subclass of MOFs, the so called MBioFs.[13] The main benefits of the nucleobases as directing units for the construction of such materials rely on their rigidity and the very well known ability to form hydrogen bonds or π–π stacking interactions, as well as on their capacity to coordinate metal ions.[14] A large number of 1-D, 2-D, and 3-D nucleobase-based coordination polymers with flexible or rigid structures and interesting properties have been reported in the literature so far.[15] However, to our knowledge, there are no examples

I

II

● = nucleobases (uracil, thymine, adenine) decorated groups

Figure 1 Target nucleobases decorated tetrasubstituted adamantane **I** and 9,9′-spirobifluorene **II** building blocks



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Dissemination of Results 2016

24. A.S. Dinca, N. Candu, S. Shova, F. Lloret, M. Julve, V.I. Parvulescu, M. Andruh, *A new chiral dimanganese(III) complex: synthesis, crystal structure, spectroscopic, magnetic, and catalytic properties*, *RSC Adv*., **2016**, *6*, 86569–86574.

25. A.A. Patrascu, S. Calancea, R.A. Allão Cassaro, S. Soriano, A.M. Madalan, C. Maxim, M.A. Novak, M.G. F. Vaz, M. Andruh, *One-dimensional coordination polymers constructed from binuclear 3d–4f nodes and isonicotinato spacer*, *CrystEngComm*, **2016**, *18*, 4779–4786.

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PAPER

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A new chiral dimanganese(III) complex: synthesis, crystal structure, spectroscopic, magnetic, and catalytic properties†

Alina S. Dinca,[a] Natalia Candu,[b] Sergiu Shova,[c] Francesc Lloret,[d] Miguel Julve,[d] Vasile I. Parvulescu*[b] and Marius Andruh*[a]

Two enantiomeric complexes of formula $[Mn_2^{III}(\mu\text{-}OCH_3)_2(R\text{-valBINAM})_2]\cdot 1.75DMF$ (1) and $[Mn_2^{III}(\mu\text{-}OCH_3)_2(S\text{-valBINAM})_2]\cdot 2DMF$ (2) [valBINAM = 1,1′-binaphthalene-2,2′-bis(3-methoxysalicylideneiminate)] have been synthesized using as a ligand the chiral Schiff bases resulting from the condensation reactions between *o*-vanillin and the chiral 1,1′-binaphthyl-2,2′-diamine. The structures of 1 and 2 which have been solved by single crystal X-ray diffraction consist of neutral dimers, the manganese(III) ions being bridged by two methoxido anions, arising from the solvent, and by two valBINAM^{2-} ligands. Their circular dichroism spectra at room temperature emphasize the occurrence of the exciton coupling effect. The cryomagnetic measurements in the temperature range 2.0–300, for compound 2, reveal the occurrence of antiferromagnetic interactions between the two Mn^{III} ions ($J = -35.5$ cm^{-1}, the Hamiltonian being defined as $H = -JS_1S_2$). The catalytic behaviour of these complexes was checked in the epoxidation of methyl *trans*-cinnamate with *N*-methylmorpholine-*N*-oxide as an oxidant. The influence of the solvent was also investigated. The reactions in a CH_3CN/H_2O (5 : 1 v/v) solvent mixture afforded total chemo- and enantioselectivity in the desired epoxides.

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Introduction

The coordination chemistry of manganese in higher oxidation states has been stimulated especially by the search for molecular magnetic materials and efficient oxidation catalysts. Indeed, manganese(III), because of its high magnetic anisotropy and large spin, is an excellent ingredient for the synthesis of molecular nano-magnets [single molecule magnets (SMMs) and single chain magnets (SCMs)].[1] On the other hand, the discovery of asymmetric epoxidation of non-functionalized olefins by chiral complexes of manganese(III) with salen-like ligands [H_2salen = *N*,*N*′-ethylenebis(salicylideneimine)] also gave a strong impulse to the development of this chemistry.[2] The salen-type ligands are readily obtained by reacting a salicylaldehide derivative with a diamine. Chiral Schiff bases from the salen family and their complexes, which are widely employed as catalysts for enantioselective reactions, can be obtained using chiral diamines.[3] One of them is the 1,1′-binaphthyl-2,2′-diamine (BINAM). A keto precursor that generates a rich variety of ligands is the *o*-vanillin.[4] Liu *et al.* have obtained chiral Schiff bases derived from *o*-vanillin and (*R*/*S*)-2-amino-1-propanol. They obtained a chiral mixed valence Mn^{II}/Mn^{III} complex by using this ligand.[5] Long *et al.* designed a chiral $[Zn^{II}Dy^{III}]$ complex using the enantiopure ligand resulting from the condensation of *o*-vanillin with 2,2′-diphenyl-ethylenediamine.[6] In this paper, we report on the synthesis of two new dimanganese(III) enantiomeric compounds of formula $[Mn_2^{III}(\mu\text{-}OCH_3)_2(R\text{-valBINAM})_2]\cdot 1.75DMF$ (1) and $[Mn_2^{III}(\mu\text{-}OCH_3)_2(S\text{-valBINAM})_2]\cdot 2DMF$ (2) [valBINAM = 1,1′-binaph-

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† Electronic supplementary information (ESI) available.
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One-dimensional coordination polymers constructed from binuclear 3d–4f nodes and isonicotinato spacer†

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Three new 1-D coordination polymers, $[Co(valpn)Gd(hfac)_2(IN)]_n$ (1), $[Ni(valpn)Gd(hfac)_2(IN)]_n$ (2), and $[Ni(valpn)Dy(hfac)_2(IN)]_n$ (3), were constructed by connecting $\{M^{II}(valpn)Ln^{III}(hfac)_2\}$ nodes through isonicotinato spacers (IN^-), with hexafluoroacetylacetonato being hfac and 1,3-propanediylbis(2-iminomethylene-6-methoxy-phenol) (H_2valpn) being the Schiff base obtained from the condensation reaction between *o*-vanillin and 1,3-diaminopropane. The synthetic approach relied on the substitution of the acetate ligands from the binuclear precursors $[M^{II}(CH_3OH)(valpn)Ln^{III}(hfac)_2(CH_3COO)]$ with the isonicotinato ligand. The investigation of the magnetic properties of all compounds showed a ferromagnetic interaction attributed to the intranode exchange interaction between the 3d and 4f metal ions. For compound 3, the AC magnetic measurements indicated a field-induced slow relaxation of the magnetization of the $[Ni^{II}Dy^{III}]$ nodes.

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Introduction

The node-and-spacer approach, first formulated by Robson as a general strategy to design coordination polymers with various dimensionalities and topologies,[1] has been expanded in scope by employing oligonuclear complexes, instead of single metal ions, as nodes.[2] The oligonuclear nodes can be either homometallic or heterometallic species. Their incorporation into extended networks occurs through one of the following routes: (i) formation of the nodes in a preliminary step, followed by the reaction with appropriate spacers;[2b,3] (ii) formation of the nodes as a result of the interaction of the metal ions with the spacer;[2a,4] or (iii) serendipitous assembly of th
metal ions into clusters, which are then interconnected t

spacer ligands.[5] We currently synthesize coordination polymers following the first synthetic approach aforementioned. The nuclearity of the potential nodes is easily controlled by employing ligands containing coordination sites that can accommodate preferentially two or more metal ions (compartmental ligand). For example, binuclear and trinuclear homometallic nodes are preformed from symmetric bicompartmental and tricompartmental ligands, which are Schiff bases resulting from the condensation reactions of various amines with 2,6-diformyl-*p*-cresol and 2,4,6-triformylphloroglucinol, respectively.[6] When heterometallic nodes are desired, dissymmetric compartmental ligands must be

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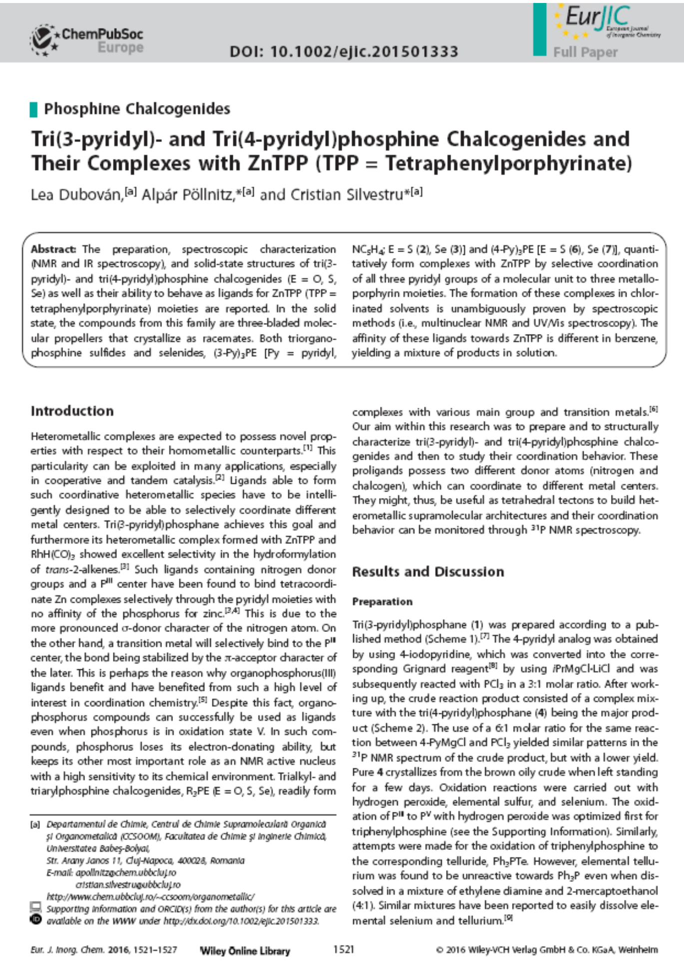
26. L. Dubovan, A. Poellnitz, C. Silvestru, *Tris(3-pyridyl)- and tris(4-pyridyl)phosphine chalcogenides and their complexes with ZnTPP (TPP = tetraphenylporphyrinate)*, *Eur. J. Inorg. Chem.* **2016,** 1521–1527.

27. M.M. Trandafir, L. Pop, N.D. Hădade, M. Florea, F. Neațu, C.M. Teodorescu, B. Duraki, J.A. van Bokhoven, I. Grosu, V. I. Pârvulescu, H. Garcia, *Adamantane-based covalent–organic framework: stability, adsorption capability, and behaviour as catalyst and support for palladium and gold for the hydrogenation of nitrostyrene*, *Catalysis Science & Technology*. **2016**, DOI:10.1039/C6CY01631F.



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Full Paper

Phosphine Chalcogenides

Tri(3-pyridyl)- and Tri(4-pyridyl)phosphine Chalcogenides and Their Complexes with ZnTPP (TPP = Tetraphenylporphyrinate)

Lea Dubován,[a] Alpár Pöllnitz,*[a] and Cristian Silvestru*[a]

Abstract: The preparation, spectroscopic characterization (NMR and IR spectroscopy), and solid-state structures of tri(3-pyridyl)- and tri(4-pyridyl)phosphine chalcogenides (E = O, S, Se) as well as their ability to behave as ligands for ZnTPP (TPP = tetraphenylporphyrinate) moieties are reported. In the solid state, the compounds from this family are three-bladed molecular propellers that crystallize as racemates. Both triorganophosphine sulfides and selenides, $(3\text{-Py})_3PE$ [Py = pyridyl, NC_5H_4; E = S (**2**), Se (**3**)] and $(4\text{-Py})_3PE$ [E = S (**6**), Se (**7**)], quantitatively form complexes with ZnTPP by selective coordination of all three pyridyl groups of a molecular unit to three metalloporphyrin moieties. The formation of these complexes in chlorinated solvents is unambiguously proven by spectroscopic methods (i.e., multinuclear NMR and UV/Vis spectroscopy). The affinity of these ligands towards ZnTPP is different in benzene, yielding a mixture of products in solution.

Introduction

Heterometallic complexes are expected to possess novel properties with respect to their homometallic counterparts.[1] This particularity can be exploited in many applications, especially in cooperative and tandem catalysis.[2] Ligands able to form such coordinative heterometallic species have to be intelligently designed to be able to selectively coordinate different metal centers. Tri(3-pyridyl)phosphane achieves this goal and furthermore its heterometallic complex formed with ZnTPP and $RhH(CO)_3$ showed excellent selectivity in the hydroformylation of *trans*-2-alkenes.[3] Such ligands containing nitrogen donor groups and a P^{III} center have been found to bind tetracoordinate Zn complexes selectively through the pyridyl moieties with no affinity of the phosphorus for zinc.[3,4] This is due to the more pronounced σ-donor character of the nitrogen atom. On the other hand, a transition metal will selectively bind to the P^{III} center, the bond being stabilized by the π-acceptor character of the later. This is perhaps the reason why organophosphorus(III) ligands benefit and have benefited from such a high level of interest in coordination chemistry.[5] Despite this fact, organophosphorus compounds can successfully be used as ligands even when phosphorus is in oxidation state V. In such compounds, phosphorus loses its electron-donating ability, but keeps its other most important role as an NMR active nucleus with a high sensitivity to its chemical environment. Trialkyl- and triarylphosphine chalcogenides, R_3PE (E = O, S, Se), readily form complexes with various main group and transition metals.[6] Our aim within this research was to prepare and to structurally characterize tri(3-pyridyl)- and tri(4-pyridyl)phosphine chalcogenides and then to study their coordination behavior. These proligands possess two different donor atoms (nitrogen and chalcogen), which can coordinate to different metal centers. They might, thus, be useful as tetrahedral tectons to build heterometallic supramolecular architectures and their coordination behavior can be monitored through ^{31}P NMR spectroscopy.

Results and Discussion

Preparation

Tri(3-pyridyl)phosphane (**1**) was prepared according to a published method (Scheme 1).[7] The 4-pyridyl analog was obtained by using 4-iodopyridine, which was converted into the corresponding Grignard reagent[8] by using *i*PrMgCl·LiCl and was subsequently reacted with PCl_3 in a 3:1 molar ratio. After working up, the crude reaction product consisted of a complex mixture with the tri(4-pyridyl)phosphane (**4**) being the major product (Scheme 2). The use of a 6:1 molar ratio for the same reaction between 4-PyMgCl and PCl_3 yielded similar patterns in the ^{31}P NMR spectrum of the crude product, but with a lower yield. Pure **4** crystallizes from the brown oily crude when left standing for a few days. Oxidation reactions were carried out with hydrogen peroxide, elemental sulfur, and selenium. The oxidation of P^{III} to P^{V} with hydrogen peroxide was optimized first for triphenylphosphine (see the Supporting Information). Similarly, attempts were made for the oxidation of triphenylphosphine to the corresponding telluride, Ph_3PTe. However, elemental tellurium was found to be unreactive towards Ph_3P even when dissolved in a mixture of ethylene diamine and 2-mercaptoethanol (4:1). Similar mixtures have been reported to easily dissolve elemental selenium and tellurium.[9]

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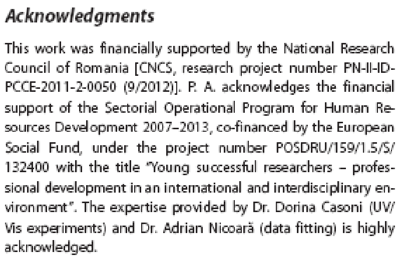

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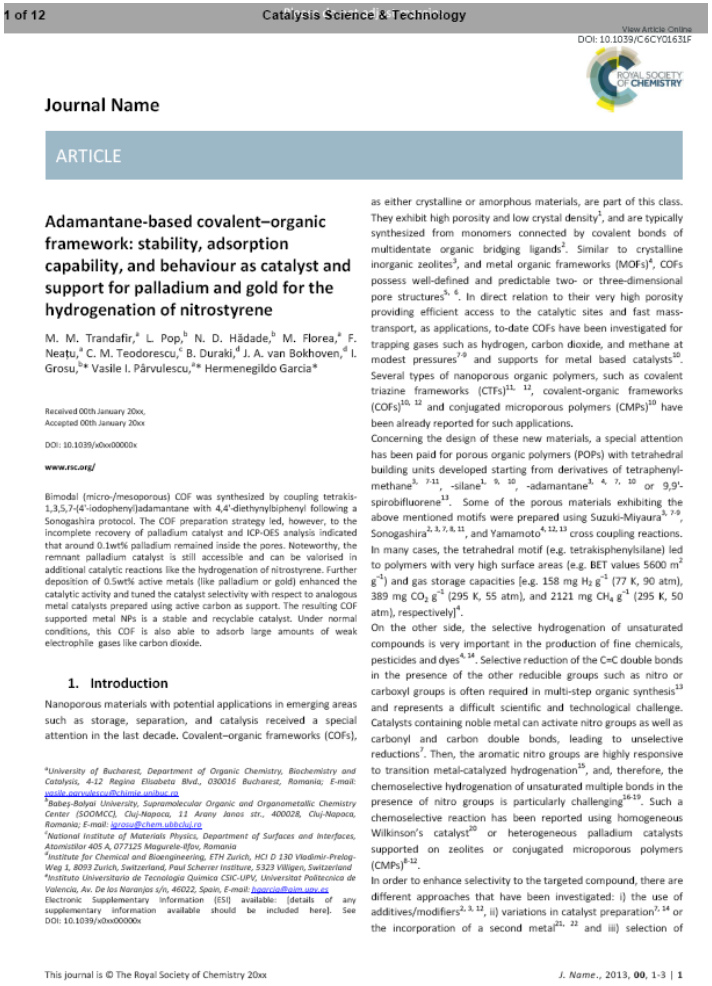

1 of 12 Catalysis Science & Technology

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ROYAL SOCIETY OF CHEMISTRY

Journal Name

ARTICLE

Adamantane-based covalent–organic framework: stability, adsorption capability, and behaviour as catalyst and support for palladium and gold for the hydrogenation of nitrostyrene

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Bimodal (micro-/mesoporous) COF was synthesized by coupling tetrakis-1,3,5,7-(4'-iodophenyl)adamantane with 4,4'-diethynylbiphenyl following a Sonogashira protocol. The COF preparation strategy led, however, to the incomplete recovery of palladium catalyst and ICP-OES analysis indicated that around 0.1wt% palladium remained inside the pores. Noteworthy, the remnant palladium catalyst is still accessible and can be valorised in additional catalytic reactions like the hydrogenation of nitrostyrene. Further deposition of 0.5wt% active metals (like palladium or gold) enhanced the catalytic activity and tuned the catalyst selectivity with respect to analogous metal catalysts prepared using active carbon as support. The resulting COF supported metal NPs is a stable and recyclable catalyst. Under normal conditions, this COF is also able to adsorb large amounts of weak electrophile gases like carbon dioxide.

1. Introduction

Nanoporous materials with potential applications in emerging areas such as storage, separation, and catalysis received a special attention in the last decade. Covalent–organic frameworks (COFs), as either crystalline or amorphous materials, are part of this class. They exhibit high porosity and low crystal density[1], and are typically synthesized from monomers connected by covalent bonds of multidentate organic bridging ligands[2]. Similar to crystalline inorganic zeolites[3], and metal organic frameworks (MOFs)[4], COFs possess well-defined and predictable two- or three-dimensional pore structures[5, 6]. In direct relation to their very high porosity providing efficient access to the catalytic sites and fast mass-transport, as applications, to-date COFs have been investigated for trapping gases such as hydrogen, carbon dioxide, and methane at modest pressures[7-9] and supports for metal based catalysts[10]. Several types of nanoporous organic polymers, such as covalent triazine frameworks (CTFs)[11, 12], covalent-organic frameworks (COFs)[10, 12] and conjugated microporous polymers (CMPs)[10] have been already reported for such applications.

Concerning the design of these new materials, a special attention has been paid for porous organic polymers (POPs) with tetrahedral building units developed starting from derivatives of tetraphenylmethane[3, 7-11], -silane[1, 9, 10], -adamantane[3, 4, 7, 10] or 9,9'-spirobifluorene[13]. Some of the porous materials exhibiting the above mentioned motifs were prepared using Suzuki-Miyaura[3, 7-9], Sonogashira[2, 3, 7, 8, 11], and Yamamoto[4, 12, 13] cross coupling reactions. In many cases, the tetrahedral motif (e.g. tetrakisphenylsilane) led to polymers with very high surface areas (e.g. BET values 5600 $m^2\,g^{-1}$) and gas storage capacities [e.g. 158 mg $H_2\,g^{-1}$ (77 K, 90 atm), 389 mg $CO_2\,g^{-1}$ (295 K, 55 atm), and 2121 mg $CH_4\,g^{-1}$ (295 K, 50 atm), respectively][4].

On the other side, the selective hydrogenation of unsaturated compounds is very important in the production of fine chemicals, pesticides and dyes[4, 14]. Selective reduction of the C=C double bonds in the presence of the other reducible groups such as nitro or carboxyl groups is often required in multi-step organic synthesis[13] and represents a difficult scientific and technological challenge. Catalysts containing noble metal can activate nitro groups as well as carbonyl and carbon double bonds, leading to unselective reductions[7]. Then, the aromatic nitro groups are highly responsive to transition metal-catalyzed hydrogenation[15], and, therefore, the chemoselective hydrogenation of unsaturated multiple bonds in the presence of nitro groups is particularly challenging[16-19]. Such a chemoselective reaction has been reported using homogeneous Wilkinson's catalyst[20] or heterogeneous palladium catalysts supported on zeolites or conjugated microporous polymers (CMPs)[8-12].

In order to enhance selectivity to the targeted compound, there are different approaches that have been investigated: i) the use of additives/modifiers[2, 3, 12], ii) variations in catalyst preparation[7, 14] or the incorporation of a second metal[21, 22] and iii) selection of

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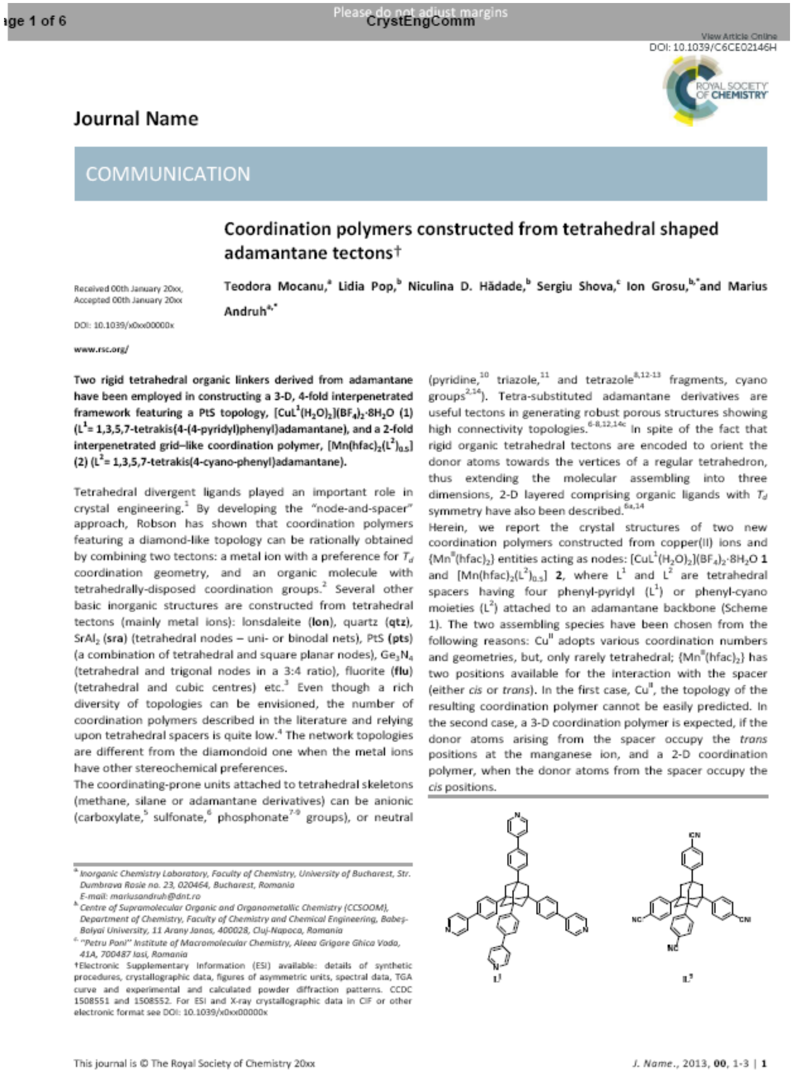
28. T. Mocanu, L. Pop, N.D. Hădade, S. Shova, I. Grosu, M. Andruh, *Coordination polymers constructed from tetrahedral shaped adamantane tectons, CrystEngComm*, **2016**, DOI: 10.1039/C6CE02146H - *accepted*.

29. A. Ilie, O. Crespo, M. C. Gimeno, M. C. Holthausen, A. Laguna, M. Diefenbach, C. Silvestru, *New (N,Se) and (Se,N,Se) ligands based on carborane and pyridine fragments. Coordination towards copper and silver, Inorg. Chem. - submitted*



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Journal Name

COMMUNICATION

Coordination polymers constructed from tetrahedral shaped adamantane tectons†

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Two rigid tetrahedral organic linkers derived from adamantane have been employed in constructing a 3-D, 4-fold interpenetrated framework featuring a PtS topology, $[CuL^1(H_2O)_2](BF_4)_2 \cdot 8H_2O$ (1) (L^1= 1,3,5,7-tetrakis(4-(4-pyridyl)phenyl)adamantane), and a 2-fold interpenetrated grid–like coordination polymer, $[Mn(hfac)_2(L^2)_{0.5}]$ (2) (L^2= 1,3,5,7-tetrakis(4-cyano-phenyl)adamantane).

Tetrahedral divergent ligands played an important role in crystal engineering.[1] By developing the "node-and-spacer" approach, Robson has shown that coordination polymers featuring a diamond-like topology can be rationally obtained by combining two tectons: a metal ion with a preference for T_d coordination geometry, and an organic molecule with tetrahedrally-disposed coordination groups.[2] Several other basic inorganic structures are constructed from tetrahedral tectons (mainly metal ions): lonsdaleite (**lon**), quartz (**qtz**), $SrAl_2$ (**sra**) (tetrahedral nodes – uni- or binodal nets), PtS (**pts**) (a combination of tetrahedral and square planar nodes), Ge_3N_4 (tetrahedral and trigonal nodes in a 3:4 ratio), fluorite (**flu**) (tetrahedral and cubic centres) etc.[3] Even though a rich diversity of topologies can be envisioned, the number of coordination polymers described in the literature and relying upon tetrahedral spacers is quite low.[4] The network topologies are different from the diamondoid one when the metal ions have other stereochemical preferences.

The coordinating-prone units attached to tetrahedral skeletons (methane, silane or adamantane derivatives) can be anionic (carboxylate,[5] sulfonate,[6] phosphonate[7-9] groups), or neutral (pyridine,[10] triazole,[11] and tetrazole[8,12-13] fragments, cyano groups[2,14]). Tetra-substituted adamantane derivatives are useful tectons in generating robust porous structures showing high connectivity topologies.[6-8,12,14c] In spite of the fact that rigid organic tetrahedral tectons are encoded to orient the donor atoms towards the vertices of a regular tetrahedron, thus extending the molecular assembling into three dimensions, 2-D layered comprising organic ligands with T_d symmetry have also been described.[6a,14]

Herein, we report the crystal structures of two new coordination polymers constructed from copper(II) ions and $\{Mn^{II}(hfac)_2\}$ entities acting as nodes: $[CuL^1(H_2O)_2](BF_4)_2 \cdot 8H_2O$ **1** and $[Mn(hfac)_2(L^2)_{0.5}]$ **2**, where L^1 and L^2 are tetrahedral spacers having four phenyl-pyridyl (L^1) or phenyl-cyano moieties (L^2) attached to an adamantane backbone (Scheme 1). The two assembling species have been chosen from the following reasons: Cu^{II} adopts various coordination numbers and geometries, but, only rarely tetrahedral; $\{Mn^{II}(hfac)_2\}$ has two positions available for the interaction with the spacer (either *cis* or *trans*). In the first case, Cu^{II}, the topology of the resulting coordination polymer cannot be easily predicted. In the second case, a 3-D coordination polymer is expected, if the donor atoms arising from the spacer occupy the *trans* positions at the manganese ion, and a 2-D coordination polymer, when the donor atoms from the spacer occupy the *cis* positions.

L^1 L^2

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† Electronic Supplementary Information (ESI) available: details of synthetic procedures, crystallographic data, figures of asymmetric units, spectral data, TGA curve and experimental and calculated powder diffraction patterns. CCDC 1508551 and 1508552. For ESI and X-ray crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

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