

Research Projects For Young Research Teams

PNII-RU-TE-2012-3-0390 (contract no. 13/26.04.2013)

Rationally designed coordination polymers as precursors for oxide nanomaterials

Project timespan: 1.05.2013 - 30.09.2016

Project Leader:

Dr. Carmen Stefanescu (Paraschiv)

Project Summary

The main goal of the present proposal is to open a new interdisciplinary research direction and to build a team of experts in both fundamental and applicative research.

We aim to develop rational synthetic strategies leading to novel metallosupramolecular architectures with pre-established structures by linking homonuclear alkoxo-bridged Zn(II) nodes into lattices with polycarboxylate and/or divergent N-donor ligands. These will be further used for the preparation of nanosized ZnO materials.

The physico-chemical properties of both precursors and ZnO particles will be investigated.

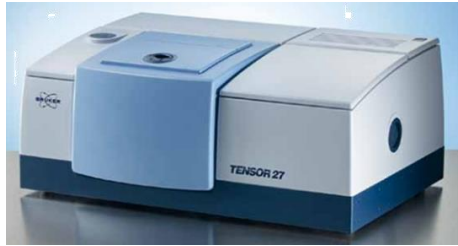
The interdisciplinary interaction of scientists with expertise in diverse areas (metallosupramolecular chemistry, synthesis of materials, materials characterization, and physics) will provide a better insight into the properties of the obtained systems.

Main objectives

- * to design and synthesize new metallosupramolecular architectures
- * to investigate the possibility of reassembling the obtained systems by solvothermal treatment in order to obtain new network topologies
- * to develop protocols for the preparation of nanosized ZnO materials from the newly synthesized compounds and to check their physico-chemical properties
- * to establish coordination polymers structural characteristics – synthetic methods – oxide features correlations
- * to investigate the parameters governing the thermal, pressure and light induced properties of compounds and search for potential applications

Main research facilities

National Institute for R&D in Electrical Engineering ICPE-CA



**Bruker TENSOR 27
FTIR Spectrometer**



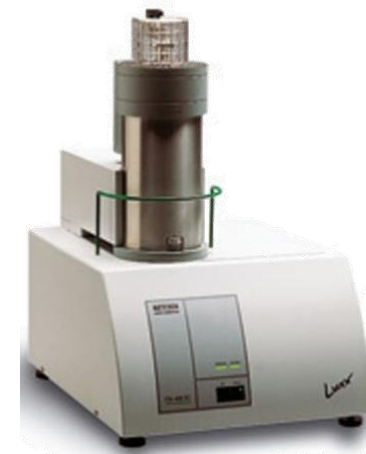
**Mettmert Humidity
chamber HCP108**



**Bruker D8 ADVANCE
Diffractometer**



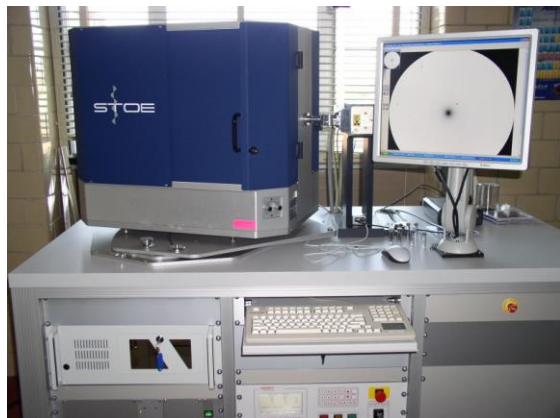
**FESEM-FIB Workstation Auriga
Carl Zeiss SMT**



**Simultaneous thermal analysis
Netzsch STA 409 PC Luxx®**

Main research facilities

University of Bucharest, Faculty of Chemistry



**STOE IPDS II X-ray
diffractometer on single-crystals**



**EuroVector EA3000
CHNS-O Elemental Analyzer**



**JASCO FP-8300
Spectrofluorimeter**

Institute of Physical Chemistry “Ilie Murgulescu”, Romanian Academy

Research team

Project leader:

Dr. Carmen-Alina STEFANESCU (PARASCHIV), Senior researcher III, National Institute for R&D in Electrical Engineering ICPE-CA

Team members:

- 1. Dr. Andrei CUCOS** Senior researcher III, National Institute for R&D in Electrical Engineering ICPE-CA
- 2. Dr. Gabriela HRISTEA** Senior researcher I, National Institute for R&D in Electrical Engineering ICPE-CA
- 3. Dr. Beatrice-Gabriela SBARCEA** Researcher, National Institute for R&D in Electrical Engineering ICPE-CA
- 4. Dr. Diana-Beatrice VISINESCU** Senior researcher II, Institute of Physical Chemistry “Ilie Murgulescu”, Romanian Academy
- 5. Dr. Catalin MAXIM** Senior researcher III, University of Bucharest, Faculty of Chemistry
- 6. Teodora MOCANU** Ph.D. student, University of Bucharest, Faculty of Chemistry*
- 7. Eng. Laura-Ileana CHIOSE** Technician, National Institute for R&D in Electrical Engineering ICPE-CA

*The Ph.D. student follows Ph.D. programs of the University of Bucharest. Her experience in the synthesis, crystallization and characterization of alkoxy-bridged systems is very useful for the project.

Conferences - 2013

1. *ZnO nanoparticles obtained by wet chemical methods*, Carmen Paraschiv, Gabriela Hristea, Gabriela Sbarcea, E-MRS Fall 2013, 16-20 september 2013, Warsaw, Poland
2. *Structural and optical properties of doped Zinc Oxide thin films*, Beatrice – Gabriela Sbarcea, Carmen Paraschiv, Jenica Neamtu, Sorina Mitrea, E-MRS Fall 2013, 16-20 september 2013, Warsaw, Poland

Conferences - 2014

1. New Zn(II) coordination polymers assembled in the presence of aminoalcohols and polycarboxylic acids. Synthesis, structure, and thermal behavior, Carmen Paraschiv, Andrei Cucos, Catalin Maxim, Augustin M. Madalan, Virgil Marinescu, The 23th Annual Symposium of the Thermal Analysis and Calorimetry Committee of the Romanian Academy, 14th February 2014, Bucharest (oral presentation)
2. New Zn(II) coordination polymers with mixed anionic linkers, Carmen Paraschiv, Andrei Cucos, Augustin M. Madalan, Catalin Maxim, 5th EUCHEMS Chemistry Congress, 31st August – 4th September 2014, Istanbul, Turkey (poster)
3. Polycarboxylate-assisted synthesis of ZnO nanoparticles, Carmen Paraschiv, Andrei Cucos, Gabriela Sbarcea, Delia Patroi, Virgil Marinescu, 5th EUCHEMS Chemistry Congress, 31st August – 4th September 2014, Istanbul, Turkey (poster)
4. A new zinc-triethanolamine-isophthalate MOF. Synthesis, crystal structure and photo-catalytic activity, Carmen Paraschiv, Andrei Cucos, Sergiu Shova, Bogdan Cojocaru, Vasile I. Parvulescu, 5th EUCHEMS Chemistry Congress, 31st August – 4th September 2014, Istanbul, Turkey (poster)
5. Alternative approaches for ZnO-graphene nanocomposites designed for supercapacitors, Gabriela Hristea, Carmen Paraschiv, Mihai Iordoc, 5th EUCHEMS Chemistry Congress, 31st August – 4th September 2014, Istanbul, Turkey (poster)

Conferences - 2015

1. *Synthesis and characterization of new Zn(II) coordination polymers constructed from amino-alcohols and aromatic dicarboxylic acids*, Carmen Paraschiv, Andrei Cucos, Sergiu Shova, Augustin M. Madalan, Catalin Maxim, The 24th Annual Symposium of the Thermal Analysis and Calorimetry Committee of the Romanian Academy, 13 February 2015, Bucharest (oral presentation)
2. *Synthesis and characterization of new Zn(II) coordination compounds constructed from amino-alcohols and divergent N-donor ligands*, Andrei Cucos, Carmen Paraschiv, Catalin Maxim, Virgil Marinescu, Sergiu Shova, Third International Conference on Advanced Complex Inorganic Nanomaterials – ACIN2015, 13 – 17 July 2015, Namur, Belgia (poster)
3. *New Zn(II) coordination polymers constructed from amino-alcohols and aromatic polycarboxylic acids*, Carmen Paraschiv, Andrei Cucos, Sergiu Shova, Third International Conference on Advanced Complex Inorganic Nanomaterials – ACIN2015, 13 – 17 July 2015, Namur, Belgia (poster)
4. *Graphene Oxide Based Nanocomposites Designed for Energy Applications*, Gabriela Hristea, Carmen Paraschiv, Mihai Iordoc, Third International Conference on Advanced Complex Inorganic Nanomaterials – ACIN2015, 13 – 17 July 2015, Namur, Belgia (poster)
5. *Synthesis, structure, TG+FTIR analysis and solid-state conversion to ZnO of new coordination compounds constructed from Zn(II), Bis-Tris and divergent N-donor ligands*, Andrei Cucos, Carmen Paraschiv, Gabriela Sbarcea, Catalin Maxim, Virgil Marinescu, Sergiu Shova, 3rd Central and Eastern European Conference on Thermal Analysis and Calorimetry (CEEC-TAC3), 25 – 29 August 2015, Ljubljana, Slovenia (poster)
6. *Synthesis and characterization of new Zn(II) extended structures based on amino-alcohols and polycarboxylic acids*, Carmen Paraschiv, Andrei Cucos, Sergiu Shova, Diana Visinescu, 19th Romanian International Conference on Chemistry and Chemical Engineering” (RICCCE 19), 2 – 5 September 2015, Sibiu, Romania (poster)
7. *Synthesis and characterization of new Zn(II) coordination compounds constructed from Bis-Tris and divergent N-donor ligands*, Andrei Cucos, Carmen Paraschiv, Catalin Maxim, Sergiu Shova, 19th Romanian International Conference on Chemistry and Chemical Engineering” (RICCCE 19), 2 – 5 September 2015, Sibiu, Romania (poster)
8. *Characterization of Zinc Oxide thin films grown on different substrates*, Gabriela Sbarcea, Carmen Paraschiv, Delia Patroi, Virgil Marinescu, Sorina Mitrea, ECM 29 – The 29th European Crystallographic Meeting, 22 – 28 August 2015, Rovinj, Croatia (poster)

Conferences - 2016

1. Coupled TG+FTIR analysis and conversion to ZnO of new coordination compounds constructed from Zn(II), amino-alcohols and divergent N-donor ligands, Cucoş A., Paraschiv C., Sbarcea G., Marinescu V., Shova S., Maxim C., XV Russian and International Conference on Thermal Analysis and Calorimetry (RTAC-2016), 19 – 23 September 2016, Sankt-Petersburg, Russia (poster)
2. Graphene hybrids designed for energy storage applications, Gabriela Hristea, Carmen Paraschiv, Mihai Iordoc, International Conference of Physical Chemistry – ROMPHYSCHEM 16, 21 – 24 September 2016, Galati, Romania (poster)
3. New Zn(II) coordination complexes as precursors for ZnO photocatalysts, Carmen Paraschiv, Andrei Cucoş, Bogdan Cojocaru, Vasile I. Pârvulescu, Marius Andruh, International Conference of Physical Chemistry – ROMPHYSCHEM 16, 21 – 24 September 2016, Galati, Romania (poster)
4. New Zn(II) coordination polymers with exo-bidentate ligands assembled in the presence of amino-alcohols, Carmen Paraschiv, Andrei Cucoş, Sergiu Shova, Cătălin Maxim, Marius Andruh, International Conference of Physical Chemistry – ROMPHYSCHEM 16, 21 – 24 September 2016, Galati, Romania (keynote lecture)

1. *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, Marius Andruh, *Cryst. Growth Des.* **2015**, 15(2), 799-811.

2. *A two-dimensional supramolecular Zn(II) system assembled via hydrogen bonds established between the terephthalate dianion and the triethanolamine ligand*, Andrei Cucos, Carmen Paraschiv, Catalin Maxim, Gabriela Sbarcea, Violeta Tudor, Marius Andruh, *Rev. Roum. Chim.* **2015**, 60(10), 997.



Article
pubs.acs.org/crystal

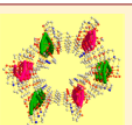
New Zn(II) Coordination Polymers Constructed from Amino-Alcohols and Aromatic Dicarboxylic Acids: Synthesis, Structure, Photocatalytic Properties, and Solid-State Conversion to ZnO

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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-benzenedicarboxylic acids in the presence of various amino-alcohols: $[Zn_2(H_2ta)_2(1,2-bdc)]$ (1), $[Zn(H_2tra)(1,3-bdc)(CH_3OH)]$ (2), $[Zn_2(H_2ta)_2(1,3-bdc)(H_2O)] \cdot 2.5H_2O$ (3), and $[Zn_2(H_2des)_2(1,4-bdc)]$ (4) (H_2ta = triethanolamine, H_2tra = tris(hydroxymethyl)aminomethane, H_2des = 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 carboxylate or alkano bridges in a helical 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 isophthalate bridges, resulting in channels of hexagonal shape, filled with water molecules. Compound 4 has a 3D structure in which linear centrosymmetric $[Zn_2(H_2des)_2]^{2+}$ 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,^{1–3} separation,^{4,5} catalysis,^{6–13} luminescence,^{14–18} recognition,^{19–23} bioactive molecules,^{24–27} and magnetism.^{28–30} 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 metal-organic linkers).^{31–33} 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 multidentate 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,^{34–36} phenolates,^{37–39} amines,^{40–42} pyridyl derivatives,^{43–45} sulfonates,^{46–47} phosphonates,^{48,49} and azolates^{50–52}). 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,⁵³ sorption,⁵⁴ separation,⁵⁵ and sensing.^{56–58}

ACKNOWLEDGMENTS

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Rev. Roum. Chim.,
 2015, 60(10), 997-1003

A TWO-DIMENSIONAL SUPRAMOLECULAR Zn(II) SYSTEM ASSEMBLED VIA HYDROGEN BONDS ESTABLISHED BETWEEN THE TEREPHTHALATE DIANION AND THE TRIETHANOLAMINE LIGAND

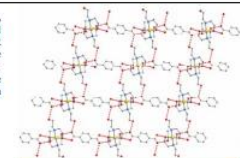
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A new mononuclear complex, $[Zn(H_2ta)_2](1,4-bdc)$ (1) (H_2ta = triethanolamine, 1,4- H_2bdc = 1,4-benzenedicarboxylic acid), was synthesized and characterized by single crystal and powder X-ray diffraction, IR spectroscopy, and thermal analysis under air atmosphere using the hyphenated TG-FTIR technique. Investigation of the crystal structure of 1 revealed a two-dimensional (2D) supramolecular motif, generated from the interconnection of $[Zn(H_2ta)_2]^{2+}$ cations and terephthalate anions through hydrogen bond interactions.



INTRODUCTION

During the last decades, significant progress has been made in understanding the nature of intermolecular interactions and their subsequent use in the formation of solid-state structures.^{1–4} The concept of the supramolecular synthon was assigned to intermolecular interactions by Desiraju in 1995,⁵ describing the association of two complementary fragments to form a motif that links two molecules together. Owing to their directionality and specificity, hydrogen bonds are the most effective and widely used non-covalent tools for the self-assembly of small molecular components into ensembles with predefined

structural features and many hydrogen-bonded motifs have been described as synthons.^{6–9} Furthermore, these supramolecular aggregates may have unique properties as a consequence of the combined features of the weakly bound entities.

Along with the coordination bond, hydrogen bonding is a key organizing force in crystal engineering due to the influence it may have on the stabilization of the lattice structure through weak interactions, e.g. between chains and layers. The

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Dissemination - Articles

3. *Interplay of hydrogen bond and stacking interactions in the crystal structure of a new mononuclear zinc complex*, Andrei Cucos, Carmen Paraschiv, Sergiu Shova, Augustin Madalan, Gabriela Sbarcea, Virgil Marinescu, Marius Andruh, *Rev. Roum. Chim.* **2015**, 60(10), 1005.



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Rev. Roum. Chim.,
2015, 60(10), 1005-1013

INTERPLAY OF HYDROGEN BOND AND STACKING INTERACTIONS IN THE CRYSTAL STRUCTURE OF A NEW MONONUCLEAR ZINC COMPLEX

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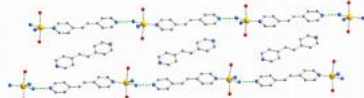
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A new mononuclear complex, $[Zn(Htris)_2(bpe)_2](NO_3)_4 \cdot 1(H_2O)$ ($H_2tris = tris(hydroxymethyl)aminomethane$, $bpe = 1,2$ -bis(4-pyridyl)ethylene), has been synthesized solvothermally. Its crystal structure, thermogravimetric analysis, solid-state transformation to ZnO and characterization of the resulted zinc oxide material are reported. The structure consists of $[Zn(Htris)_2(bpe)_2]^{2+}$ mononuclear dicationic species, uncoordinated bpe molecules and nitrate anions. The crystallographic investigation reveals the formation of one-dimensional chains based upon N-H...N hydrogen bond interactions between the amino nitrogens coordinated to the zinc atoms and the bpe ligand from an adjacent mononuclear entity. The π - π stacking interactions established between the aromatic fragments of the coordinated and uncoordinated bpe molecules also play an important role in sustaining the supramolecular solid-state architecture. Furthermore, a 3-D supramolecular network is formed through plentiful hydrogen bonds involving the ligands, the guest molecules and the nitrate counteranions.



INTRODUCTION

Metal directed formation of molecules is governed by the coordination geometry of the metal ion and influenced by various non-covalent forces, mainly originating from the structural features of the ligands. Hydrogen bonds and π - π stacking interactions are important supramolecular tools that can contribute to a fast and reversible assembly of molecules and have been encountered in numerous systems reported so far.^{1,2}

Rigid rod-like molecules have been widely employed as tectons in supramolecular chemistry and crystal engineering. Among them, aromatic

nitrogen containing ligands such as 4,4'-bipyridine³ and bis(4-pyridyl) derivatives (e.g. 1,2-bis(4-pyridyl)ethane,⁴ 1,2-bis(4-pyridyl)ethylene,⁵ bis(4-pyridyl)acetylene,⁶ 1,4-bis(4-pyridyl)benzene⁷) have been used for the construction of numerous coordination polymers with various dimensionalities and network topologies. These molecules can act as ligands (bridging or monodentate) or can be found as guests in the crystal lattice. At the supramolecular level, they

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4. *Two Zn(II) distortion isomers in a single crystal. Synthesis, supramolecular interactions and thermal analysis*, Carmen Paraschiv, Andrei Cucos, Sergiu Shova, Marius Andruh, *Rev. Roum. Chim.*, **2016**, 61(4-5), 311-317.



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Rev. Roum. Chim.,
2016, 61(4-5), 311-317

Dedicated to Professor Alexandru T. Balaban
on the occasion of his 85th anniversary

TWO Zn(II) DISTORTION ISOMERS IN A SINGLE CRYSTAL. SYNTHESIS, SUPRAMOLECULAR INTERACTIONS AND THERMAL ANALYSIS

Carmen PARASCHIV,^{a*} Andrei CUCOS,^a Sergiu SHOVA^b and Marius ANDRUH^c

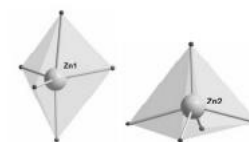
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A new mononuclear complex, $[Zn(Htris)_2(1,3-bde)] \cdot 1(H_2O)$ ($H_2tris = tris(hydroxymethyl)aminomethane$, $1,3-bde = 1,3$ -benzenedicarboxylic acid), was synthesized solvothermally and characterized by single crystal and powder X-ray diffraction, IR spectroscopy, and thermal analysis under synthetic air atmosphere using the coupled TG-FTIR method. The asymmetric unit contains two distortion isomers. Slight variations in the bond lengths and angles within the chromophores impose different geometries for the zinc atoms in the two isomers. The 3D supramolecular networks, formed through plentiful H-bonds and weak molecular interactions, has been analyzed.



INTRODUCTION

The past decades have witnessed tremendous progress in crystal engineering.¹ One of the challenges is to improve our understanding of how the balance between strong/weak forces determines the assembly of the molecules in the crystal. Hydrogen bonding is undoubtedly the most efficient and widely used non-covalent tool for molecular self-assembly by reason of its strong directing capability, selectivity and reversible formation at room temperature.² The O-H...O hydrogen bonds formed by -COOH and -OH groups are among the strongest non-covalent interactions. Furthermore, the

O-H...O bond can be strengthened if the polarity of the acceptor is increased via deprotonation of the carboxylic group. These interactions are sufficiently strong to influence recognition and self-assembly of carboxylic acid/carboxylate anions in high dimensional superstructures.³

Nowadays hydro- or solvothermal synthesis is one of the most popular methods to obtain coordination networks despite the fact that the synthetic target is not always reached and chance and serendipity often affect the outcome of the reaction.⁴

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