Development of Novel Tunable Porous Materials: Design, Synthesis, Characterization, and Applications

Financial support: UEFISCDI



Project Code: PN-II-RU-PD-2012-3-0528 (project 21 - 26/04/2013) Project timespan: 01.05.2013 - 30.10.2015

Project Leader: Dr. Delia – Laura Popescu Mentor: Acad. Marius Andruh

Summary

The project aims to provide a rational design for the synthesis of novel tunable MOFs, to study their porous properties, and to prove their efficiency in applications, such as catalysis, gas storage, separations, sensing, luminescence, magnetism, etc. New families of di- and trimetallic complexes will be synthesized and used as tectons for MOFs with desired network topologies. A variety of organic ligands, such as hydroxy-acids and amino-acids will be employed, special attention being given to chiral organic ligands to obtain systems that can be used as tectons for chiral MOFs. The ability of different organic and metal-organic species to act as spacers will be tested in the process of self-assembly of MOFs. Post-synthesis processes will be performed to improve the catalytic properties of the obtained coordination polymers. The sorption of various gases (H2, CH4, CO2, C2H2, etc.) and the catalytic properties of the synthesized MOFs will be investigated. The ability of the new obtained MOFs to act as adsorbents for gaseous pollutants and molecules resulted from degradation of pharmaceutical and pesticides compounds will be tested. Enantioselective organic reactions catalyzed by chiral MOFs as well as stereoselective separations will be studied. The luminescent and magnetic properties of some MOFs as well as the influence of the host molecules on these properties will be investigated.

Objectives

The general objective of the project is to provide a rational design for the synthesis of novel tunable MOFs, to study their porous properties, and to prove their efficiency in applications, such as catalysis, gas storage, separations, sensing, luminescence, magnetism, etc.

The main goals derived from the general objective are:

- 1. Design, synthesis and characterization of new families of metal complexes as tectons for MOFs with desired network topologies.
- 2. Building MOFs based on the newly designed and synthesized metal complexes employed as nodes.
- 3. Optimization of MOFs architectures based on the design improvement of new spacers and nodes.
- 4. Optimizing MOFs properties by post-synthesis processes.
- 5. Testing the synthesized MOFs for emerging applications, such as: selective sorption capacity, gas storage, asymmetric catalysis and stereoselective separations, luminescence, magnetism, etc.



3. Long, J.R., Horike S., Dincă M., Tamaki K., J. Am. Chem. Soc, 2008, 130, 5854





PROJECT BUDGET

Budget chapter	2013	2014	2015	Total
(expenses)	(lei)	(lei)	(lei)	(lei)
Salaries	70000	80000	22727.3	172727.3
Inventory	50000	25000	0	75000
Mobility	15000	10000	0	25000
Overhead	13500	11500	2272.7	27272.7
Total	148500	126500	25000	300000

Articles



Atmospheric CO₂ capture by a triphenyltin-1,2-bis(4-pyridyl)ethane system with formation of a rare trinuclear carbonato-centered core

Alina-Elena Ghionoiu ", Delia-Laura Popescu **, Catalin Maxim ", Augustin M. Madalan ", Ionel Haiducha, Marius Andruh **

ABSTRACT

 Introduction Chamberry Laboratory Residence Chamberry of Recharger, Str. Dumbrave Rook nr. 22, 020064 Bacharger, Romania * Fasily of Chemistry and Chemical Engineering, "Index-Boly d" (Internity, Cul-Hapora, Remarks

ARTICLE INFO

Article history Received 2 April 2015 Received in revised thrm 26 May 2015 Accepted 3 kine 2015 Available online 6 kine 2015

Organistin(N) Tripud ear carbonate-cantered core

Keywentic Carlson di oxide capture

upramole cula r structure

Direct atmospheric CD₂ captum occurred during the reactions of triphenyltin diloride (Ph₂SnCI) with 1,2bis (4-ppr id) (b) these (bp.a) in methanol and aqueous ammonia. Depending on the maction temperature, $4^{-1}C$ and more temperature, two different compounds were obtained: a discrete, trituclear complex, $((\beta h_{3} \circ G)_{2})_{2} + CO_{3}((\beta h_{3} \circ G)$ CO3)(bp a)]-H2O (2), respectively. X-Nay crystal structure analysis reveals that both compounds contain a rare trinuclear carbo nato-ombred core C/OSePh_b. The supramolecular architecture of compound L assembled by hydrogen-b and interactions, a described.

© 2015 Elsevier BV All rights manyed.

around the carbonato a nion. To the best of our know indge, the only sin-

ilar case is the formation of I/Ph-Sn}-(CD-YEtOH)-J-Cl-(ntb) H-O.

CrossMark

The capture of atmospheric carbon dioxide, a major greenhouse gas, is of great current interest: therefore, various methods to reduce the COlevels 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 CD₂ insertion into Sn-O bonds is facile in the alkouide series and compounds exhibiting a C(OSnR₃)₃ core with R = CH₂, C₄H₂, *C₄H₂, as well as some polymenic organotin carbonates are known [4].

out ammonia an alkaline environment that favors the canture of CO. 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 relation temperatures. Thus, at 4 °C, atrinuciear mplex, [(Ph₃SnCl)₂(µ_e-CD₃)(Ph₃Sn)(Hbpa)]-H₂O(1)[6], was isolat-

ed, whereas at mom temperature (ca 25 °C) a 1-D coordination polymer, 1_J(Ph_SoC1)(Ph_So)_J(µ_r CO_3)(bpa)]-H_2O (2), was obtained [7]. Both compounds were investigated by single crystal X-ray diffrac

tion [8] and were found to contain a trinuclear unit, C(OSoPh, h, built

E-mail addresse: drillapoge natilizējyshon.com(D.-J. Ropercej, italikusējazidzo (I. Haidac), markutandrubiēdnizo (M. Andrubi).

We report here an unexpected capture of atmospheric carbon dioxide which occurred during the reaction of triphenyltin chioride (Ph_SnO) with 1,2-bis(4-pyridyl)ethate (bpa), in methanol and aque-

where nth - tris(2-benzinidazoly)-methyl)amine, obtained from PhySnC1 NaOEt and ntb in open atmosphere. In this compound the trinuclear units formed around the (D), group are nodes connected into a 3D supramolecular network linked through OH"N bonds [9]. Crystallographic analysis reveals that compound 1 crystalizes in the monoclinic centrosymmetric space group P2, /c The molecular structure of compound 1 is shown in Fig. 1. The central CO₂ group coordinates



Fig. 1. The molecular structure of [(Ph,SnG)_j(µ-CO_1)(Ph,Sn)(Hipa)]; H₂O, compound 1 with partial numbering othernes. All H atoms are conitted for clarity. The H atom which protocome N2 is not shown. Alina-Elena Ghionoiu. Delia-Laura Popescu.* Catalin Maxim, Augustin M. Madalan, lonel Haiduc,* Marius Andruh*, ATMOSPHERIC CO₂ CAPTURE BY A TRIPHENYLTIN-1,2-BIS(4-**PYRIDYL)ETHANE SYSTEM WITH FORMATION** A RARF TRINUCLEAR CARBONATO-OF CENTERED CORE. Chemistry Inorganic Communications, 2015, 58, 71-73. DOI: 10.1016/j.inoche.2015.06.003

Acknowledgments

Financial support of this work by the Romanian Executive Agency for Higher Education, Research, Development and Innovation (UEFISCDI) through the grants PN-II-ID-PCCE-2011-2-0050 and PN-II-RU-PD-2012-3-0528 is gratefully acknowledged.

http://dudolorg/10.1016/.inoche2015.06.003 1387-7003/0.2015 Elsevier R.V. All rights reserved

· Conceptualing authors

Conferences

1). <u>Delia-Laura Popescu</u>, Mihaela Mocanu, Augustin M. Mădălan, Cătălin Maxim, Marius Andruh, **RATIONAL DESIGN, SYNTHESIS, AND STRUCTURAL CHARACTERIZATION OF NOVEL COPPER(II) EXTENDED STRUCTURES,** The 18th Romanian International Conference on Chemistry and Chemical Engineering – RICCCE18, Sinaia, Romania, 3-8 septembrie 2013 (oral presentation)

2). Oana Dorina Neagu, Mihaela Mocanu, Cătălin Maxim, Delia-Laura Popescu,* Marius Andruh*, **NEW 1,2-BIS(4-PYRIDYL)ETHANE-BRIDGED COPPER(II) COORDINATION POLYMERS,** The 12th International Conference "Students for Students", Cluj-Napoca, Romania, 22-26 aprilie 2015 (oral presentation)

Conferences

3). Gabriela Andreea Manda, **Delia-Laura Popescu**,* Catalin Maxim, Ionel Haiduc, Marius Andruh*, **NEW POLINUCLEAR ORGANOTIN(IV) SYSTEMS: SYNTHESIS AND STRUCTURAL CHARACTERIZATION**, The 12th International Conference "Students for Students", Cluj-Napoca, Romania, 22-26 aprilie 2015 (oral presentation)

4). Mihaela Mocanu, **Delia-Laura Popescu**,* Cătălin Maxim, Augustin M. Mădălan, Marius Andruh*, **RATIONAL DESIGN AND STRUCTURAL CHARACTERIZATION OF THREE NOVEL EXTENDED STRUCTURES OF COPPER(II),** ZILELE Universității "Alexandru Ioan Cuza" din Iași, Conferința FACULTĂȚII DE CHIMIE, Iasi, Romania, 29-31 octombrie 2015 (oral presentation)

Conferences

5. NEW POLYNUCLEAR SYSTEMS DERIVED FROM ORGANOTIN COMPOUNDS

Alina-Elena Ghionoiu, **Delia-Laura Popescu**,^{*} Cătălin Maxim, Ionel Haiduc, Marius Andruh^{*}, *A XXXIII-a Conferință Națională de Chimie, cu participare internațională*, 1-3 Oct. **2014** Călimănești-Căciulata, Vâlcea, Romania.



6. COORDINATION POLYMERS CONTAINING MONO- AND BINUCLEAR Cu(II)-HYDROXYCARBOXILATO NODES

Oana Dorina Neagu, Elena Mădălina Bărbuc, Cătălin Maxim, **Delia-Laura Popescu***, Marius Andruh*, *A XXXIII-a Conferință Națională de Chimie, cu participare internațională,* 1-3 Oct. **2014** Călimănești-Căciulata, Vâlcea, Romania.



Conferences



7. SYNTHESIS AND CHARACTERIZATION OF NEW EXTENDED STRUCTURES BASED ON Cu(II) AND DICARBOXYLIC ACIDS

Silvana Vasilca, **Delia-Laura Popescu,*** Cătălin Maxim, Marius Andruh*, *A XXXIII-a Conferință Națională de Chimie, cu participare internațională,* 1-3 Oct. **2014** Călimănești-Căciulata, Vâlcea, Romania.

Research Stages

1). 26.09.2014 – 7.12.2014 in Prof. Dr. Christoph Janiak's group at University of Düsseldorf, Institute for Inorganic Chemistry and Structural Chemistry, 40204 Düsseldorf, Germany.

2). 10.08.2015 – 30.09.2015, in Prof. Dr. Christoph Janiak's group at University of Düsseldorf, Institute for Inorganic Chemistry and Structural Chemistry, 40204 Düsseldorf, Germany.