

RELANSIN -CEEX 016 (2005-2008)

CALIXARENES BASED COMPOSITE MATERIALS WITH MAGNETIC AND/OR SELECTIVE COMPLEXATION PROPERTIES FOR SOME METALLIC IONS OF TECHNOLOGICAL INTEREST-CALIXCOM

Project manager: dr. Elisabeth-Jeanne Popovici

CONSORTIUM

Coordinator :

CO-P1- Institute for Research in Chemistry, Cluj-Napoca, **ICRR**

Partners:

P2- Politehnica University Bucharest, Faculty of Chemical Engineering –Bucharest, **UPB**
(prof. dr. Doru Nechifor)

P3- Babes Bolyai University Cluj-Napoca, Faculty of Chemistry and Chemical Engineering, Cluj-Napoca, **UBB**
(prof.dr. Ioan Silaghi-Dumitrescu, m.c. Al Academiei Romane);

P4- National Institute of R&D for Isotopical and Molecular Technologies, Cluj-Napoca, **INCOTIM**
(dr. Nicolae Palibroda);

P5- INCDO-INOE2000, branch Institute for Research in Analytical Instrumentation, Cluj-Napoca **ICIA**
(Bella Abraham);

P6- University of Medicine and Pharmacy “Iuliu Hatieganu” –UMF, Faculty of Pharmacy, Cluj –Napoca, **UMF**
(conf.dr. Radu Opreanu)

Programmed results

■ Consortium structure

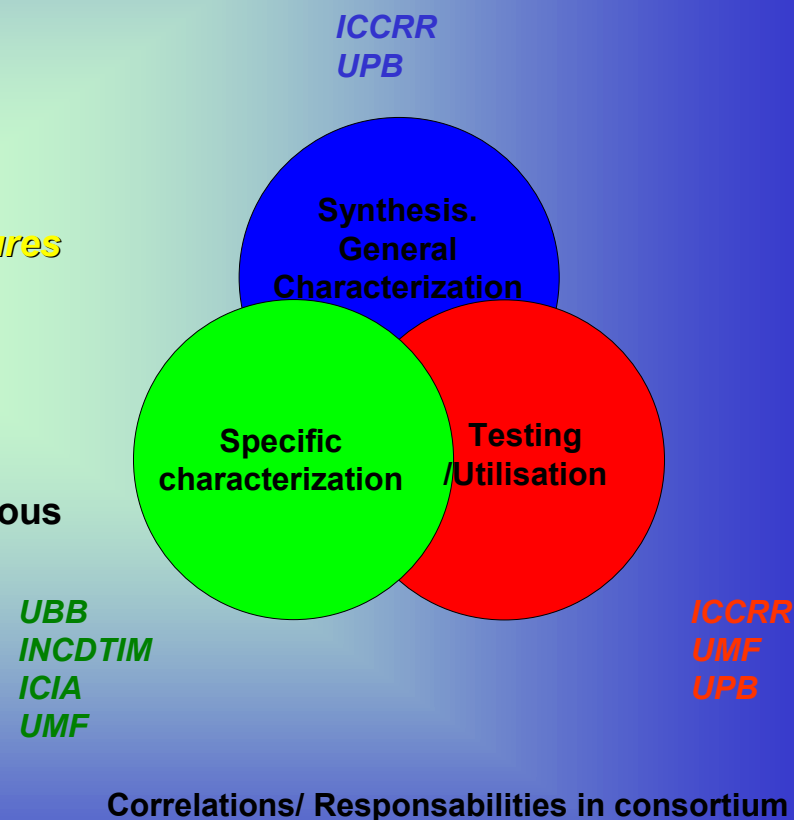
- ICCRR-Cluj (dr. E.J.Popovici)
- UPB-Bucuresti (prof.dr. D.Nechifor);
- UBB-Cluj (prof.dr. Ioan Silaghi-Dumitrescu)
- INCDTIM-Cluj (dr. N. Palibroda)
- ICIA-Cluj (chim.Bella Abraham);
- UMF-Cluj (conf.dr. R. Opreanu)

■ Technical-scientific results ⇒ *technologies; products; procedures*

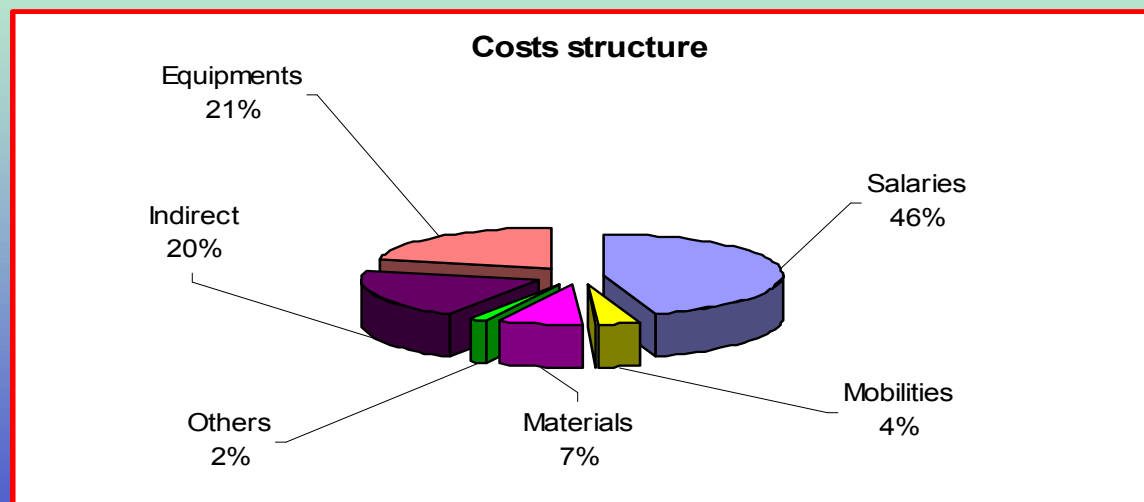
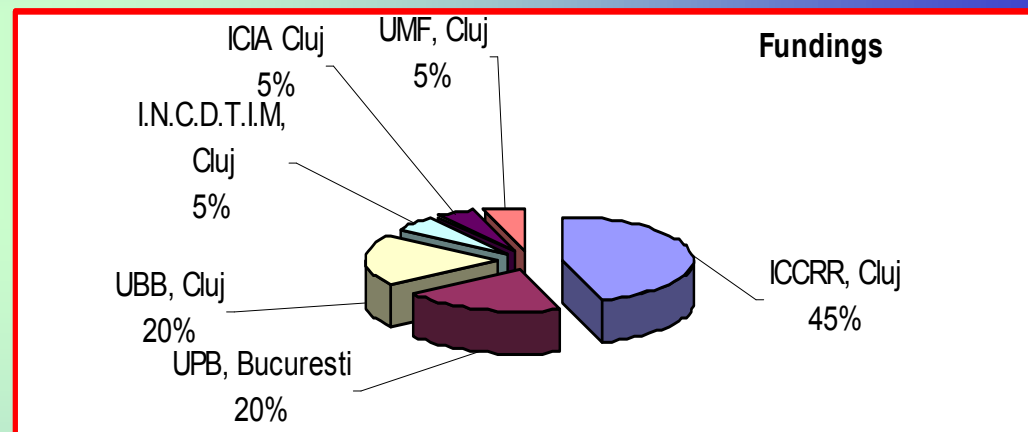
- Micro-composite material CALIXCOM-A
- Nano-composite material CALIXCOM- H ;
- Separation/Extraction of rare earth (RE) / precious metal (PM) ions with CALIXCOM-A
- Separation/Extraction of metallic ions with CALIXCOM-H
- Extraction of metallic ions of technological interest from aqueous medium

■ Results dissemination

- Published works (papers);
- Works presented to scientific manifestations
- Organisation of one thematic Workshop
- Patent(s)



Fundings/ Costs structure



General objective of the project

Preparation of some new calixarene-based micro- and nanostructured materials with magnetic properties and/or selective complexation ability of some ions of technical interest

⇒ *microcomposite material CALIXCOM-A = composite powder based on adsorbent-calixarene system*

⇒ *hybrid nanocomposite material CALIXCOM-H = suspension of nanoparticles functionalised with calixarene, with magnetical properties*

Project plan

1st Stage (2005). Scientific-technical fundamentation of the project. Preliminary studies ⇔ Partners: ICCRR, UPB, UBB, INCDTIM, UMF

2nd Stage (2006). Researches referring to the synthesis of some new products based on chemically modified calixarenes ⇔ Partners: ICCRR, UPB, UBB, INCDTIM, ICIA, UMF

3rd Stage (2006). Studies referring to the evaluation of the capability of chemically modified calixarenes to coordinate metallic ions of technical interest ⇔ Partners: ICCRR, UPB, UBB, INCDTIM, ICIA

4th Stage (2007). Researches regarding the preparation and characterisation of hybrid and adsorption composite materials based on calixarenes ⇔ Partners: ICCRR, UPB, UBB, INCDTIM, UMF

5th Stage (2008). Studies referring to the utilisation of the CALIXCOM-type materials for the separation/isolation from aqueous medium of metals of technical interest ⇔ Partners: ICCRR, UPB, UBB, INCDTIM, ICIA, UMF

Project progress

Performed researches

- Studies referring to the synthesis and characterisation of some new compounds based on para-tert-butyl-calix[4]arene and para-tert-butyl-calix[6]arene, obtained by grafting of some functional groups with increased co-ordination potential, products that are to be used for the preparation of the adsorption-based micro-composite material *CALIXCOM-A* (*Annex 1*)
- Studies referring to the preparation of nanoparticles as well as to the synthesis and characterisation of some chemically modified calix[4]arene, the components of the hybrid nanocomposite material *CALIXCOM-H*

Up-to-now results

- Consolidation of the material basis of partners :
 - a) *R&D Equipments* : **Thermal Analyser*: TG-DTG-SDTA system and DSC colorimeter (Mettler-Toledo); Colloidal mill with accessories; Automatique applier for plan separations;
 - b) *Laboratory instruments/ devices*;
 - c) *PC equipments, soft-wares*
- Basic researches in the field of calixarenes. Results disseminations. (*Annex 2*);
- Preparation of some product sets, component parts of *Calixcom A* and *Calixcom H*, that are to be tested as complexation agents.

New para *t*-butyl-calix[6]arene for rare earth ions extraction

N. Popovici, E.-J. Popovici, A.Saponar, I. Silaghi-Dumitrescu, D.Nechifor, R. Oprean & N. Palibroda

Introduction

■ Paper goal

➤ Synthesis of some new chemically modified calixarene with increased capability to coordinate RE^{3+} ; Derivatization was performed at the "narrow rim", with crotyl groups $CH_3-HC=CH-CH_2-$ (π electrons) and amido $[-CH_2-CO-NR_2]$ and ester $[-CH_2-COO-R]$ or both (p electrons)

■ General presentation of calixarenes

- Polynuclear compounds obtained through condensation of alkyl-phenols with formaldehyde;
- Compounds with host-guest properties, their characteristic feature being a shape cavity whose dimension can be modified with the use of grafted groups;
- Compounds with specific structure that allows them to function as supramolecular receptors of cations, anions or neutral molecules.

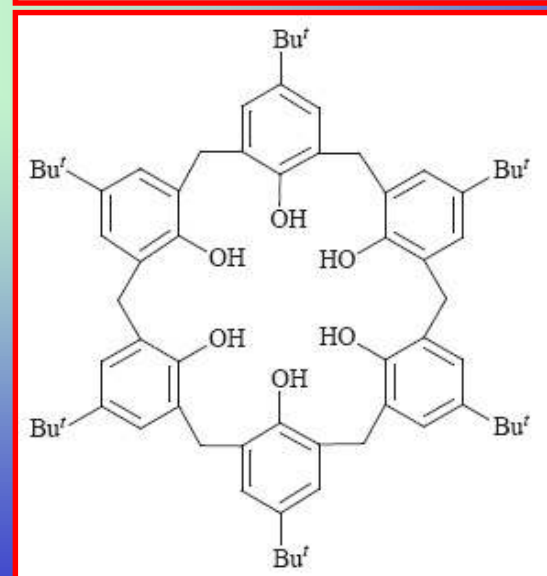
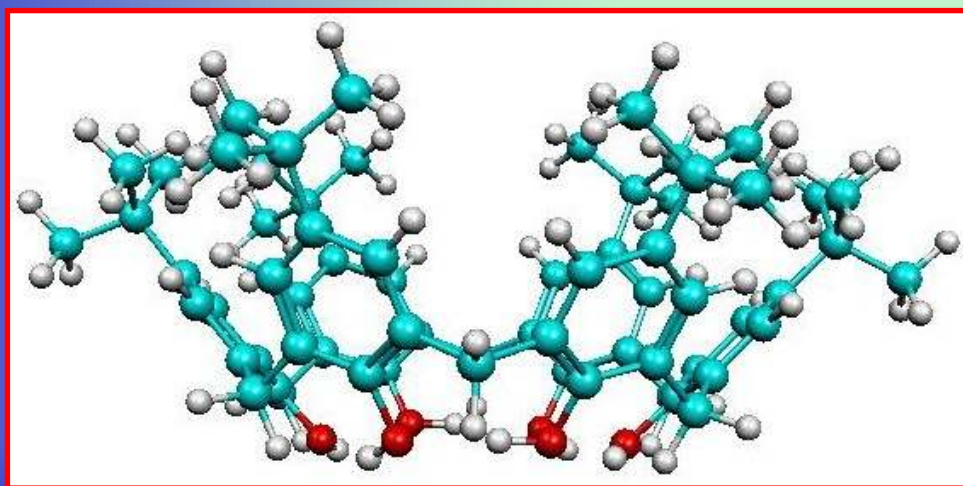
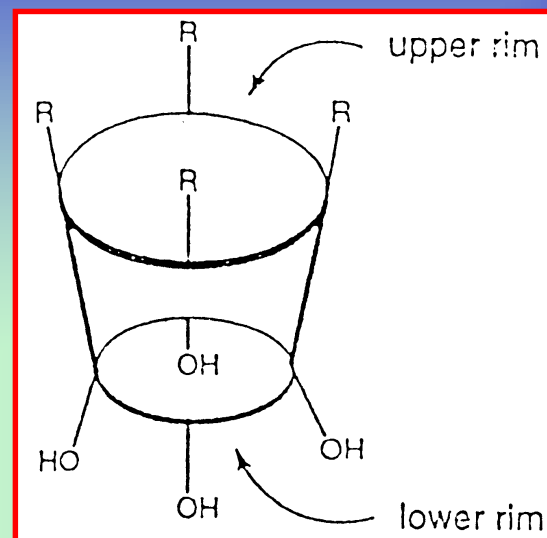
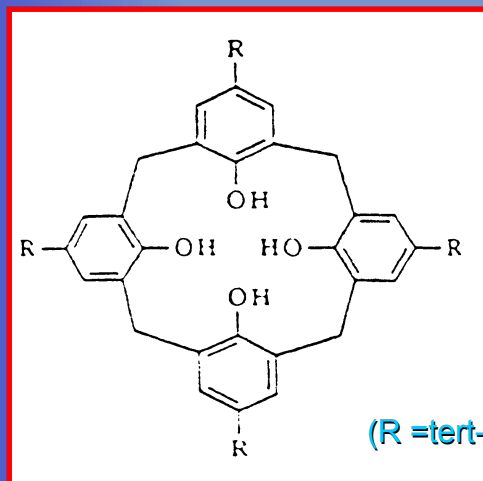
■ General requests for the use of calixarenes as receptors/extracting agents from metals from aqueous medium

- To contain polar groups capable to replace the hydration shell (sphere) of ions that are to be complexed
- To present the coordination possibility through donor grafted groups;
- To show a large solubility in non-polar solvents and to be insoluble in water;
- The calixarene cavity has to have an optimal dimension to trap the target ions;
- To form a complex that has to remain in the membrane phase;
- Complex formation has to be rapid and irreversible.

■ Synthesis pathway

para-*t*-butyl phenol \Rightarrow para-*t*-butyl calix[4,6]arene \Rightarrow para-*t*-butyl-calix[4,6]arene derivative

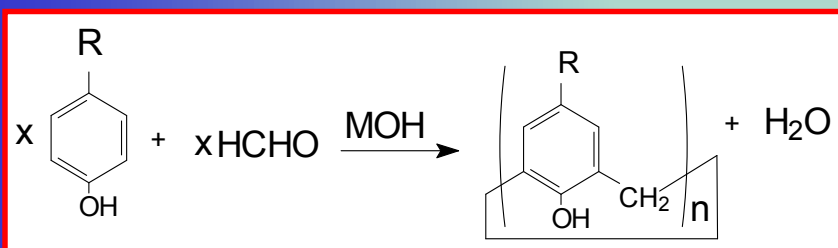
Schematic representation of the compounds p-tert-butyl calix[4]arene and p-tert-butyl calix [6]arene



Experimental part

Preparative stages

a) Preparation of the parent calix[6]arene



where

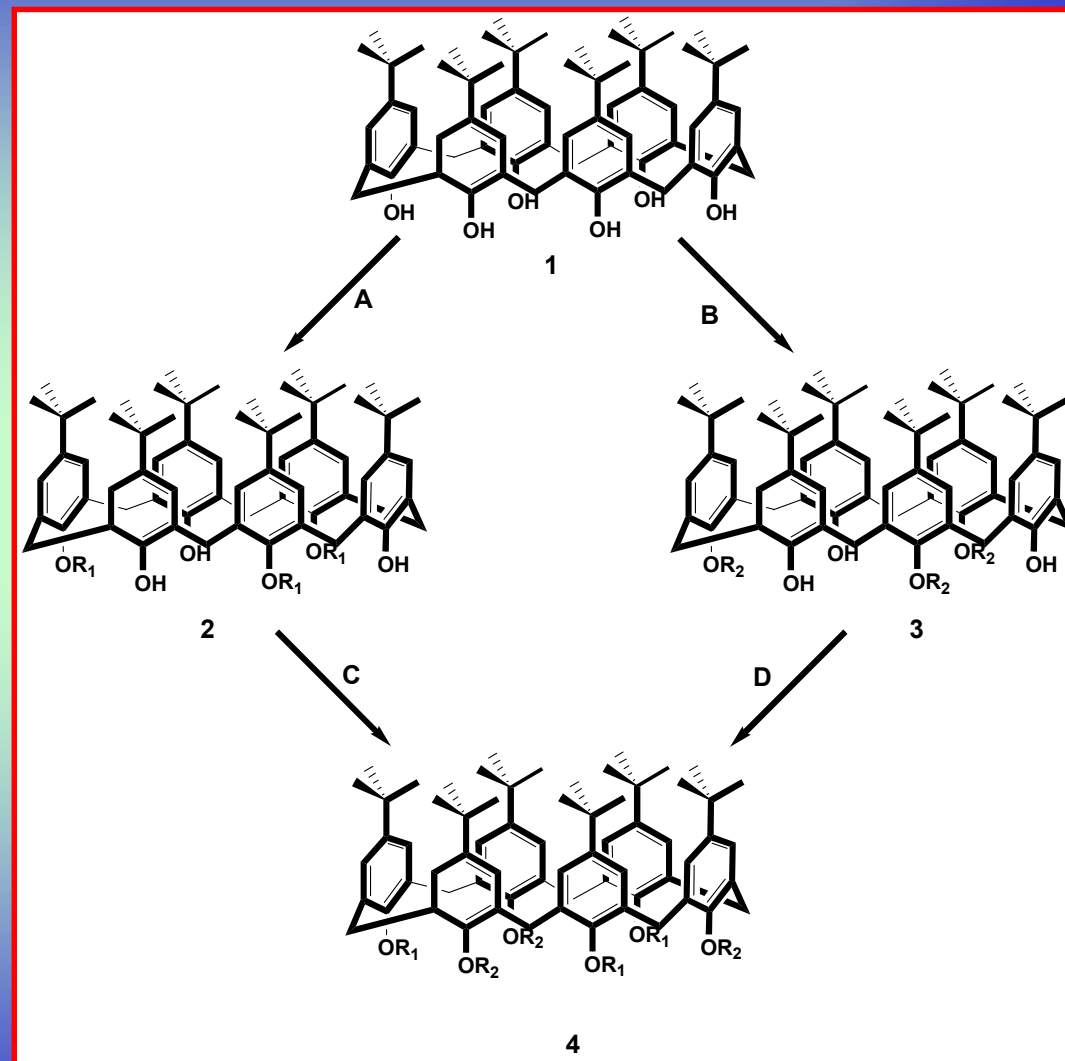
$x = 4, 6, 8$; $n = 4; 6; 8$; $M = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$.

b) Synthesis of the functionalised calixarene

Compound 2 \Leftrightarrow **C6Cr3, p-tert-butyl-tricrotyl-trihidroxi calix[6]arene**

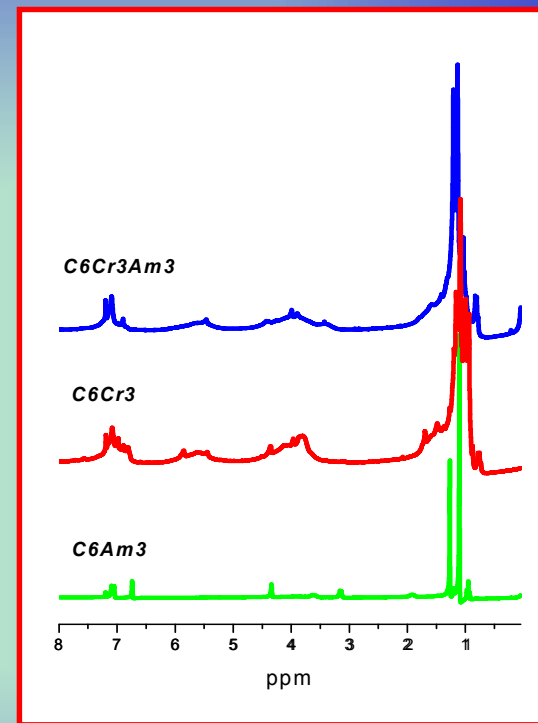
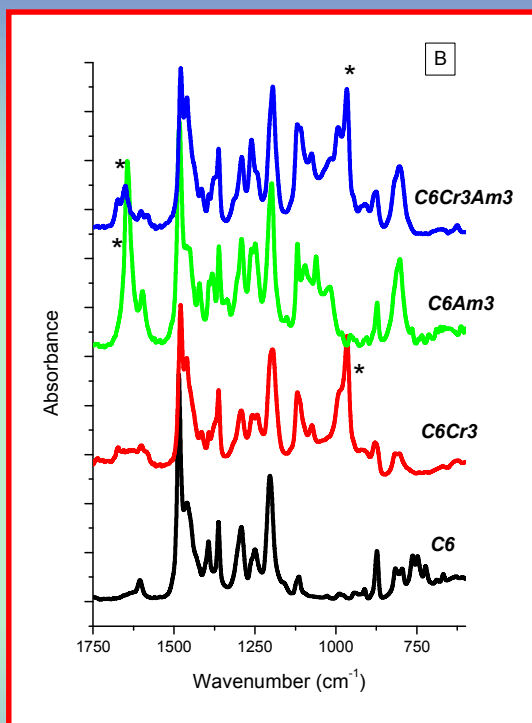
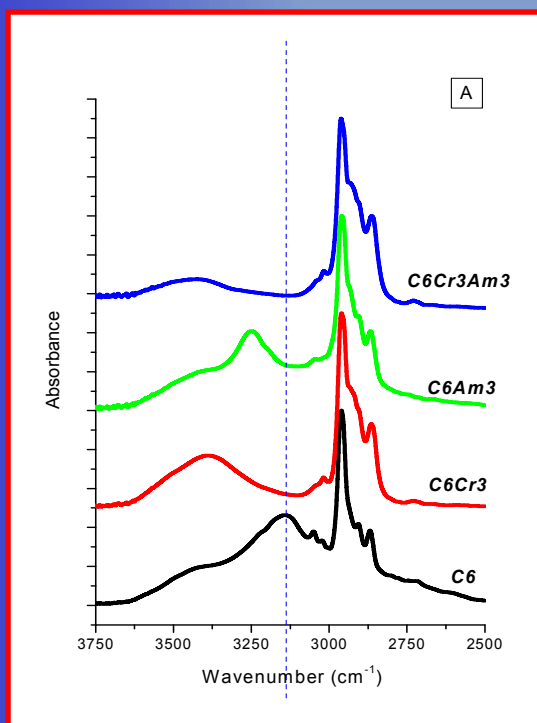
Compound 3 \Leftrightarrow **C6Am3, p-tert-butyl -triamido-trihidroxi calix[6]arene**

Compound 4 \Leftrightarrow **C6Cr3Am3, p-tert-butyl -tricrotyl-triamido calix[6]arene**



Results

Characterisation by FTIR spectroscopy and ¹H-RMN spectroscopy



Conclusions

- The chosen pathway enabled the preparation of C6Cr3, C6Am3, C6Cr3Am3 derivatives;
- The synthesis yield of the calixarene derivative with mixed groups C6Cr3Am3 is relatively low;
- Researches are in progress for: * Optimization of the synthesis procedure of the calix[6]arene with mixed substituting groups; * Testing the derivatives capability to extract/complexate RE and PM ions.

Results dissemination

Communicated / published results

- *“Towards novel coupling agents containing unsaturated organogermane fragments”, G. Nemes, J. Escudié, I. Silaghi-Dumitrescu, H. Ranaivonjatovo, L. Silaghi-Dumitrescu, H. Gornitzka ⇔ „International Conference on Organometallic Chemistry XXII” Zaragoza, Spania, 22 iulie-28 iulie 2006;*
- *“The interplay between tetrahedrane, butterfly diradical, and planar rhombus structures in $fe_2(co)_6(\mu-x)_2$ chemistry (X = S, PR; R = H, Me, tBu, OR', NR', Cl)” Ioan Silaghi-Dumitrescu, R. Bruce King, and Thomas E. Bitterwolf ⇔ „International Conference on Organometallic Chemistry XXII” Zaragoza, Spania, 22 iulie-28 iulie 2006;*
- *“New calix[n]arene derivatives for rare earth ions extraction” A. Saponar, E.-J. Popovici, I.Silaghi-Dumitrescu, R. Grecu, N. Popovici ⇔ “1st European Chemistry Congress- Budapest , 27-31 Aug 2006”;*
- *“Synthesis of Calix[6]Arene Derivatives Substituted at The “Narrow-Rim” A.Saponar, E.-J.Popovici, I.Silaghi-Dumitrescu, N.Popovici ⇔ 5th International Conference of the South-East European Chemical Societies- ICOSECS5-Ohrid, Macedonia, 10-14 sept 2006;*
- *“Synthesis and Spectral Characterisation of New Calix[4]pyrogalolarenes”, N.Popovici, T.-N. Ursales, N. Palibroda, I.Silaghi-Dumitrescu, A. Saponar & E.-J. Popovici⇔ 5th International Conference of the South-East European Chemical Societies- ICOSECS5-Ohrid, Macedonia,10-14 sept 2006;*
- *“Studii privind extractia sinergetica a cationilor alcalini Na^+ si K^+ in prezenta unor amestecuri p-terbutilcalix[4]arena –eteri coroana ” M. Bumbac, B. Serban, C. Lucac, G. Nechifor, V. Stefan (REVISTA DE CHIMIE, submitted)*
- *Synthesis and characterization of calix[4]arene with different donor groups at the “narrow” rim, A. Saponar, I Silaghi-Dumitrescu, E-J Popovici, and N. Popovici, (REVISTA DE CHIMIE, submitted)*
- *„Noi derivați de tert-butyl-calix[6]arenă pentru extractia ionilor de pământuri rare” (N.Popovici, E.-J.Popovici , A.Saponar, I.Silaghi-Dumitrescu, R.Oprean și N.Palibroda), Volumul de lucrări al Conferinței,, Cercetarea de excelență-premisă favorabilă pentru dezvoltarea spațiului românesc de cercetare”, 22-24 oct. 2006 Brasov; L1-21/1-6.*