
INORGANIC AND ORGANOMETALLIC CHEMISTRY

Annual Activity Report 2013

UNIT: Chemical and Radiopharmaceutical Sciences

TEAM

Name	Category	R&D (%)
Joaquim Marçalo	Principal Researcher	100%
João Paulo Leal	Auxiliary Researcher (habilitation)	100%
Joaquim B. Branco	Auxiliary Researcher	100%
José Manuel Carretas	Auxiliary Researcher	100%
Teresa Almeida Gasche	Auxiliary Researcher	100%
Cláudia C.L. Pereira*	Auxiliary Researcher (Ciência 2007)	100% (Jan-Feb)
Leonor Maria	Auxiliary Researcher (Ciência 2008)	100%
Adelaide Cruz	Graduated Technician	100%
Bernardo Monteiro	Post-doc (FCT grant)	100% (July-Dec)
Ana F. Lucena	PhD student (FCT grant)	100%
Ana C. Ferreira	PhD student (FCT grant)	100%
Cybelle Soares	Research student (FCT project grant)	100% (Sept-Dec)
Vânia Sousa	Research technician (FCT grant)	100%
Marina Soares	Research student (FCT project grant; CQE-IST)	100%
Maria Augusta Antunes	Post-doc (FCT grant; ES-UCQR)	50%
Joana M. Vitorino	PhD student (FCT grant; CQB-FCUL)	30%
Ana Moura	Research student (FCT grant; UFA)	10% (July-Dec)

*Ceased in 28-02-2013.

OBJECTIVES

- The research activities of the **Inorganic and Organometallic Chemistry Group** are centred on the study of several aspects of the **chemistry of f-elements** (lanthanides and actinides) at fundamental and applied levels, with focus on topics of relevance in **environmental, nuclear and materials sciences**.
- The activities comprise the **synthesis** of new compounds and materials, **reactivity and catalysis** studies, and examination of **structural, optical and magnetic properties**. Different aspects of the chemistry of **elementary species** are examined using **molecular mass spectrometry**. The investigation of the **thermodynamic properties** of key species in **condensed and gas phases** is pursued, as is the development of methods for the **prediction** of relevant thermodynamic properties.

These activities are developed under four major subjects:

- **Coordination and organometallic chemistry** - Synthesis of complexes with new coordination environments and hybrid materials (metal-organic frameworks, layered hydroxides and ionic liquids) to be examined for their chemical, magnetic and optical properties, searching for unusual or enhanced behaviour.
- **Heterogeneous catalysis** - Preparation of nanostructured intermetallic and bimetallic oxides with d-block elements, and their study as catalysts or catalyst precursors in heterogeneous phase for the activation of methane, carbon dioxide and nitrogen oxides.

- **Gas-phase chemistry** - Identification of new molecular species and study of the chemical properties of key species, namely hydration, hydrolysis, redox behaviour, and complexation interactions with model molecules, using FTICR and QIT mass spectrometry.
- **Molecular energetics** - Collection of energetics data of organic and inorganic compounds using calorimetry, thermal analysis and mass spectrometry, and development of databases and prediction models of thermochemical properties.

MAIN ACHIEVEMENTS

Coordination and Organometallic Chemistry

[Collaborations: GES-UCQR; REQUIMTE-FCT/UNL; CQE-IST; CICECO-U. Aveiro; St. Petersburg State U., CEA-Grenoble.]

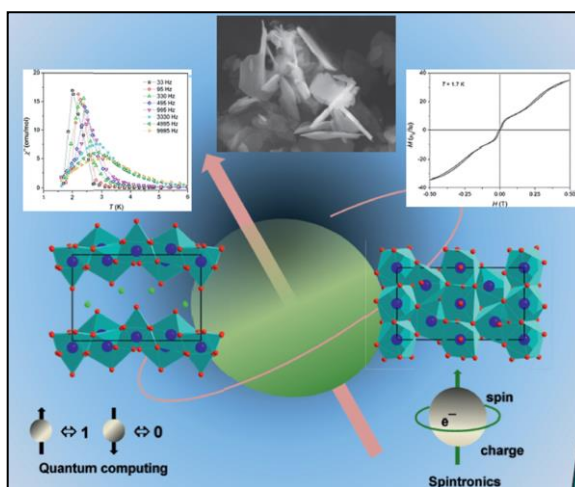
New Sm(III) complexes supported by a diamine bis(phenolate) ligand were prepared and structurally characterized, including a complex with a Sm-C bond.

New complexes of Sm(II) and Yb(II) with ancillary functionalized aza-macrocyclic ligands were prepared and reactivity studies toward redox active substrates initiated.

The chemistry of the U(III) complex $[U\{(Ar^{t-Bu}O)_2Me_2-Cyclam\}I]$ continued to be examined and allowed the stabilization of different U complexes in the oxidation states +3 to +6.

New U(III) complexes with N-donor ligands were synthesized, structurally characterized and their reactivity with small molecules and behaviour as single-molecule magnets examined.

The synthesis and characterization of Layered Lanthanide Hydroxides and their intercalation products continued, and the luminescence and magnetic properties of these materials studied. $Dy_8(OH)_{20}Cl_4 \cdot 6H_2O$, the first example of a layered lanthanide compound with SMM behaviour, a joint work of QIO and ES Groups, was reported and the cover of an issue of the European Journal of Inorganic Chemistry.



New uranyl and thorium Metal-Organic Frameworks based on phosphonate ligands were synthesized and their structural properties examined.

Ionic Liquids involving anionic Ln(III) tetrakis(β -diketonate) complexes and a tetraalkylphosphonium as counter-ion were prepared and their luminescence and magnetic properties scrutinized.

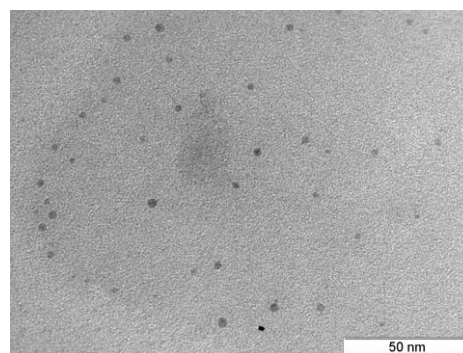
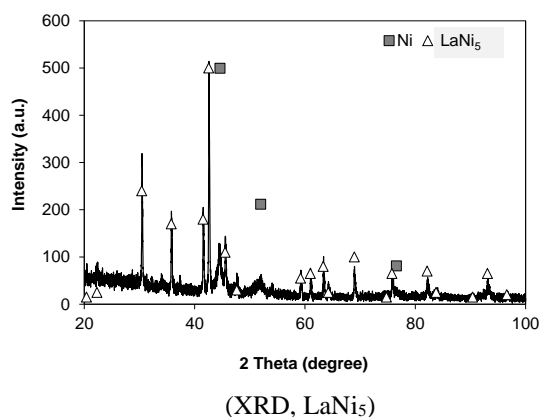
Heterogeneous Catalysis

[Collaborations: GES-UCQR; CQFM-IST; ISQ; FCUL.]

Nanoparticles of d- and f-block intermetallic compounds (e.g. $LaNi_5$) and bimetallic oxides (e.g. $Ca-An-O$, $An=Th, U$) were obtained using a sol-gel method and properly characterized for the first time, and their chemical properties evaluated in the activation of CH_4 and CO_2 as C1 feedstocks and N_2O as oxidant, either for the production of syngas or C2 hydrocarbons.

A new method, electrospinning, was used to successfully produce nanoparticles of intermetallic compounds containing f-block elements (e.g. $LaNi_5$, $LaCu_2$, $SmCo_5$ and $DyFe_3$).

The development of a high pressure continuous reactor (type flow reactor) for methane and carbon dioxide activation studies, aiming at the production of alcohols, was initiated.



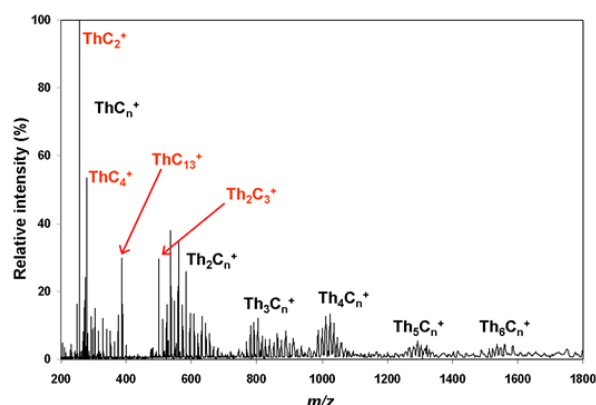
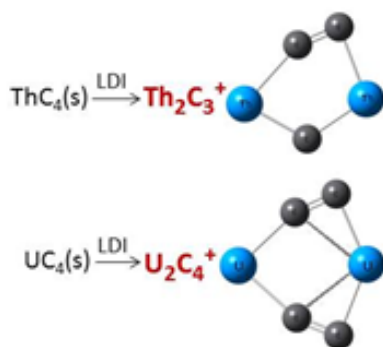
(TEM, Ca-Th-O)

Gas-phase Chemistry

[Collaborations: LBNL, U. Calabria, GES-UCQR.]

LDI-FTICR/MS and ESI-QIT/MS were used to explore the chemical properties of elementary actinide species: the properties of thio-uranyl, $\{S=U^{VI}=S\}^{2+}$, as examined by experiment and theory, were reported; O₂-addition to uranyl(V) species of the type $[UO_2X_2]$ to form superoxo complexes was studied in detail for different X⁻ anions.

The formation of molecular Th and U carbide clusters by laser ionization of solid metal carbides was reported; a disparity between Th and U in the relative abundances of the bimetallic ions $An_2C_3^+$ and $An_2C_4^+$ was elucidated by DFT based computations.



ESI-QIT/MS was used to examine the interactions of actinyl ions with amino-acids and nucleobases, in an attempt to understand fundamental aspects of the bio-inorganic chemistry of the actinides.

Molecular Energetics

[Collaboration: CQB-FCUL.]

Enthalpies of formation of several diol compounds were determined and the corresponding reactivity and catalytic properties assessed.

The ThermoInfo database (<http://www.thermoinfo.com>) was improved, including in a new release much more compounds and properties; also, new models for properties prediction (both for ionic compounds and covalent organic ones) were developed.

Other Activities

- Studies of low temperature gas discharges for the activation of CH₄ and CO₂ (collab. UFA).
- Gas-phase chemistry studies of *d*-transition metals (collab. CQE-IST).
- Studies of the degradation of bio-recalcitrant compounds (collab. UFA).
- Studies of hybrid materials for biomedical applications (collab. UFA).
- Chemistry for Education activities at the Chemistry and Biochemistry Department of FCUL.

The Group members were **co-authors** in: 13 publications in WoS journals (plus 8 in press or accepted), 1 EU patent, 1 publication in other journals, 1 publication in conference proceedings, 3 other publications, and 30 communications in conferences.

A **new FCT project** was initiated in July 2013: “CO₂ mitigation and production of methanol by reforming of CH₄” - PTDC/AAG-TEC/3324/2012. Members of the Group are in the **teams of 3 FCT projects** initiated in 2013: “Increasing the energy efficiency of plasma conversion of methane” - PTDC/FIS-PLA/2135/2012 (Leader UFA); “Application of ionizing radiation for a sustainable environment” - RECI/AAG-TEC/0400/2012 (Leader UFA); “From drug design to new materials: structural approach in emergent fields” - RECI/QEQ-QIN/0189/2012 (Leader CQE-IST).

The Group participates in the **FCT Doctoral Programme CATSUS** - Catalysis and Sustainability (PD/00248/2012; <http://catsus.tecnico.ulisboa.pt/>), led by CQE-IST.

RELEVANT PUBLICATIONS

- J.M. Carretas, S. Barroso, J. Cui, A. Cruz, I.C. Santos, A.M. Martins, Diamine bis(phenolate) samarium complexes: syntheses and structures, *Inorganica Chimica Acta*, 407, 175-180 (2013), DOI: 10.1016/j.ica.2013.07.051.
- L. Maria, I.C. Santos, L.G. Alves, J. Marçalo, A.M. Martins, Rare earth metal complexes anchored on a new dianionic bis(phenolate)dimethylamine-cyclam ligand, *Journal of Organometallic Chemistry*, 728,57-67 (2013), DOI: 10.1016/j.jorganchem.2012.12.026.
- C.C.L. Pereira, S. Dias, I. Coutinho, J.P. Leal, L.C. Branco, C.A.T. Laia, Europium(III) tetrakis(β-diketonate) complex as an ionic liquid – a calorimetric and spectroscopic study, *Inorganic Chemistry*, 52, 3755-3764 (2013), DOI: 10.1021/ic3023024.
- B. Monteiro, C.C.L. Pereira, J.T. Coutinho, L.C.J. Pereira, J. Marçalo, M. Almeida, A 2D layered lanthanide hydroxide showing slow relaxation of magnetization – Dy₈(OH)₂₀Cl₄•6H₂O, *European Journal of Inorganic Chemistry*, 5059–5063 (2013), DOI: 10.1002/ejic.201300793.
- C.C.L. Pereira, R. Maurice, A.F. Lucena, S. Hu, A.P. Gonçalves, J. Marçalo, J.K. Gibson, L. Andrews, L. Gagliardi, Thorium and uranium carbide cluster cations in the gas phase: similarities and differences between thorium and uranium, *Inorganic Chemistry*, 52, 10968–10975 (2013), DOI: 10.1021/ic401058b.

FUNDS

Project/Service	Reference	Timeframe	2013
CO ₂ mitigation and production of methanol by reforming of CH ₄	PTDC/AAG-TEC/3324/2012	01.07.2013-30.06.2015	23.010,60 €
Chiral metalla-diaminocarbene precatalysts for asymmetric catalytic reactions obtained by the metal-mediated approach	PTDC/QUI-QUI/109846/2009	01.04.2011-31.09.2014	2.497,24 €
Gas-phase thermochemistry of 4d and 5d transition metal oxides: a study by FTICR-MS	PTDC/QUI-QUI/108977/2008	01.01.2010-31.12.2012	709,13 €
RNEM: National Mass Spectrometry Network	IST/ITN Node	01.01.2013-31.12.2013	2.300,00 €
EUFEN: European f-Element Network	COST Action CM1006	19.04.2011-18.04.2015	1.800,00 €
Total			30.316,97

TEAM RESEARCHERS

NAME: Joaquim Carrasqueiro Marçalo de Almeida

CATEGORY: Principal Researcher

IST-ID: 5365

ACTIVITIES

Nº	Activity Description	R&D (%)
1	Gas-phase chemistry/mass spectrometry of lanthanides and actinides	30
2	Coordination and organometallic chemistry of lanthanides and actinides	20
3	Functional hybrid materials with f-elements	15
4	Coordination of the Inorganic and Organometallic Chemistry Group	15
5	Supervision of post-docs, PhD students and research students	10
6	Services to the community	10
Total		100

WORK SUMMARY

Nº	Work Summary and Main Achievements
1	<p><i>Gas-phase chemistry and thermochemistry of elementary actinide species:</i> LDI-FTICR/MS and ESI-QIT/MS were used to explore the chemical properties of elementary actinide species (An = Th-Cm). [Performed by PhD student A.F. Lucena and researcher J.M. Carretas.]</p> <p><i>Gas-phase chemistry of actinides with biomolecules:</i> ESI-QIT/MS was used to examine the interactions of actinyl ions with amino-acids and nucleobases, in an attempt to understand fundamental aspects of the bio-inorganic chemistry of actinides. [Performed by PhD student A.F. Lucena and “Ciência-2008” researcher L. Maria.]</p> <p>[Collaborations with J.K. Gibson (LBNL); M.C. Michelini (U. Calabria); A.P. Gonçalves (GES-UCQR).]</p>
2	<p><i>Uranium complexes with functionalized aza-macrocyclic ligands:</i> The chemistry of the U(III) complex [U{(Ar^{t-Bu}2O)₂Me₂-Cyclam}I] continued to be examined and allowed the stabilization of different U complexes in the oxidation states +3 to +6. [Performed by “Ciência-2008” researcher L. Maria that also supervised and technician A. Cruz.]</p> <p><i>Lanthanide complexes with functionalized aza-macrocyclic ligands:</i> New Ln(II) (Sm, Yb) complexes with [(Ar^{R2}O)₂Me₂-Cyclam]²⁻ (R = Me, t-Bu) as ancillary ligands were prepared and reactivity studies toward redox active substrates initiated. [Performed by “Ciência-2008” researcher L. Maria that also supervised and research student M. Soares.]</p> <p><i>Uranium complexes with N-donor ligands – reactivity and magnetic properties:</i> New U(III) complexes with N-donor ligands were synthesized, structurally characterized and their reactivity with small molecules and behavior as single-molecule magnets examined. [Performed by post-doc M.A. Antunes (GES-UCQR).]</p> <p>[Collaborations with K. Luzyanin (St. Petersburg State U.); I.C. Santos, L.C. Pereira, M. Almeida, (GES-UCQR); M. Mazzanti (CEA-Grenoble); H. Bolvin (U. Paul Sabatier-Toulouse III).]</p>
3	<p><i>Layered Lanthanide Hydroxides:</i> The synthesis and characterization of Layered Lanthanide Hydroxides (LLHs) and their intercalation products continued, and the luminescence and magnetic properties of these materials studied. [Performed by post-doc B. Monteiro and “Ciência-2007” researcher C.C.L. Pereira.]</p> <p><i>Metal-Organic Frameworks of the actinides:</i> New uranyl and thorium Metal-Organic Frameworks (MOFs) based on phosphonate ligands were synthesized and their structural properties examined. [Performed by post-doc B. Monteiro and “Ciência-2007” researcher</p>

	C.C.L. Pereira.] <i>Multifunctional Ionic Liquids with lanthanides</i> : Ionic Liquids (ILs) involving anionic Ln(III) tetrakis(β -diketonate) complexes (Ln = Dy, Gd, Tb) and a tetraalkylphosphonium as counter-ion were prepared and their luminescence and magnetic properties scrutinized. [Performed by post-doc B. Monteiro, "Ciência-2007" researcher C.C.L. Pereira and researcher J.P. Leal.] [Collaborations with L.C. Pereira, M. Almeida (GES-UCQR); F. Almeida-Paz (CICECO-U. Aveiro); J.C. Lima, C.A.T. Laia, I. Coutinho (REQUIMTE-FCT/UNL)].
4	The coordination of the Inorganic and Organometallic Chemistry Group involved typical tasks of such an occupation.
5	Supervision of post-doc B. Monteiro (FCT grant SFRH/BPD/47087/2008, Jul-Dec 2013) and PhD student A.F. Lucena (FCT grant SFRH/BD/70475/2010, Jan-Dec 2013, co-supervisors J.K. Gibson/LBNL and J.P. Leal/FCUL) within the research activities described in 1-4. Supervision of technical research student V. Sousa (FCT grant SFRH/BTI/51253/2010, Jan-Dec 2013, co-supervisor J. Branco) in CHNS elemental analysis (UCQR service).
6	Support to other research groups of UCQR through ca. 70 MS analyses (ESI-QIT and EI/LDI-FTICR) of organic compounds and metal complexes. Support to UCQR in the management of gases and cryogenic liquids.

PUBLICATIONS

- L. Maria, I.C. Santos, L.G. Alves, J. Marçalo, A.M. Martins, Rare earth metal complexes anchored on a new dianionic bis(phenolate)dimethylaminecyclam ligand, *Journal of Organometallic Chemistry*, 728, 57-67 (2013), DOI: 10.1016/j.jorgchem.2012.12.026.
- E. Mora, L. Maria, B. Biswas, C. Camp, I.C. Santos, J. Pécaut, A. Cruz, J.M. Carretas, J. Marçalo, M. Mazzanti, Diamine bis(phenolate) as supporting ligands in organoactinide(IV) chemistry. Synthesis, structural characterization, and reactivity of stable dialkyl derivatives, *Organometallics*, 32, 1409–1422 (2013), DOI: 10.1021/om3010806.
- B. Villeroy, A.P. Goncalves, G. Delaizir, C.C.L. Pereira, J. Marçalo, X. Wang, L. Andrews, C. Godart, Preparation of dense C-13 pellets using spark plasma sintering technique, *Materials Research Innovations*, 17, 289-292 (2013), DOI: 10.1179/1433075X12Y.0000000062.
- M.A. Antunes, I.C. Santos, H. Bolvin, L.C.J. Pereira, M. Mazzanti, J. Marçalo, M. Almeida, Crystal structure diversity in the bis[hydrotris(3,5-dimethylpyrazolyl)borate]iodouranium(III) complex: from neutral to cationic forms, *Dalton Transactions*, 42, 8861-8867 (2013), DOI: 10.1039/c3dt50753j.
- C.C.L. Pereira, R. Maurice, A.F. Lucena, S. Hu, A.P. Gonçalves, J. Marçalo, J.K. Gibson, L. Andrews, L. Gagliardi, Thorium and uranium carbide cluster cations in the gas phase: similarities and differences between thorium and uranium, *Inorganic Chemistry*, 52, 10968–10975 (2013), DOI: 10.1021/ic401058b.
- B. Monteiro, C.C.L. Pereira, J.T. Coutinho, L.C.J. Pereira, J. Marçalo, M. Almeida, A 2D layered lanthanide hydroxide showing slow relaxation of magnetization – Dy₈(OH)₂₀Cl₄•6H₂O, *European Journal of Inorganic Chemistry*, 5059–5063 (2013), DOI: 10.1002/ejic.201300793.
- C.C.L. Pereira, M.C. Michelini, J. Marçalo, Y. Gong, J.K. Gibson, Synthesis and properties of uranium sulfide cations. An evaluation of the stability of thiouranyl, {S=U=S}²⁺, *Inorganic Chemistry*, 52, 14162–14167 (2013), DOI: 10.1021/ic4020493.

COMMUNICATIONS

- *Precursors for Submicron and Nanostructured Uranium Carbides*, M.S. Henriques, A. Cruz, M. Kratochvílová, J. Marçalo, L. Havela, T. Stora, A.P. Gonçalves, *43èmes Journées des Actinides, Sestri Levante, Italy, Apr 6-9 (2013)*, Poster.
- *Micro and Nanostructured Lanthanide Carbides Prepared by Electrospinning*, M.S. Henriques, A. Cruz, M. Kratochvílová, J. Marçalo, A. Rudajevová, L. Havela, T. Stora, A.P. Gonçalves, *EUFEN2 - Meeting of COST Action CM1006: European f-Element Network, Dublin, Ireland, Apr 17-18 (2013)*, Oral.

- *Crystal Structure Diversity in $[U(Tp^{Me_2})_2I]$ - From Neutral to Cationic Forms*, M.A. Antunes, I.C. Santos, H. Bolvin, L.C.J. Pereira, M. Mazzanti, J. Marçalo, M. Almeida, *EUFEN2 - Meeting of COST Action CM1006: European f-Element Network, Dublin, Ireland, Apr 17-18 (2013)*, Poster.
- *Formation and Dissociation of Uranyl-, Neptunyl- and Plutonyl-Glycine Complexes in the Gas Phase*, A.F. Lucena, L. Maria, Y. Gong, J.K. Gibson, J. Marçalo, *EUFEN2 - Meeting of COST Action CM1006: European f-Element Network, Dublin, Ireland, Apr 17-18 (2013)*, Poster.
- *Oxygen Addition Reactions of Uranyl(V) Complexes in the Gas Phase*, A.F. Lucena, J.M. Carretas, Y. Gong, M.C. Micheline, J.K. Gibson, J. Marçalo, *EUFEN2 - Meeting of COST Action CM1006: European f-Element Network, Dublin, Ireland, Apr 17-18 (2013)*, Poster.
- *Uranyl Metal-Organic Frameworks Based on Phosphonate Ligands*, C.C.L. Pereira, B. Monteiro, J.A. Fernandes, F.A. Almeida Paz, J. Marçalo, *EUFEN2 - Meeting of COST Action CM1006: European f-Element Network, Dublin, Ireland, Apr 17-18 (2013)*, Poster.
- *Uranium Complexes Supported by Bis-phenolate Tetraazacyclotetradecane: Insight into the Reactivity of a New Uranium(III) Compound*, L. Maria, I.C. Santos, A. Cruz, J. Marçalo, *EUFEN2 - Meeting of COST Action CM1006: European f-Element Network, Dublin, Ireland, Apr 17-18 (2013)*, Poster.
- *Ln(III) Tetrakis(β -diketonate) Complexes (Ln(III) = Dy, Gd, Tb) as Multifunctional Ionic Liquids*, B. Monteiro, L.C.J. Pereira, I. Coutinho, J.P. Leal, J. Marçalo, C.A.T. Laia, C.C.L. Pereira, *XXIII Encontro Nacional da Sociedade Portuguesa de Química, Aveiro, Portugal, Jun 12-14 (2013)*, Poster.
- *Divalent Lanthanide Complexes Supported by Bis(phenolate) Cyclam Ligands*, L. Maria, E. Mora, V. Sousa, I.C. Santos, K.V. Luzyanin, J. Marçalo, *20th EuCheMS Conference on Organometallic Chemistry, St. Andrews, Scotland, Jun 30–Jul 4 (2013)*, Poster+Flash Oral.
- *Submicron and Nanostructured Uranium Carbides Prepared by Electrospinning*, M.S. Henriques, A. Cruz, J. Marçalo, L. Havela, T. Stora, A.P. Gonçalves, *Actinides 2013, Karlsruhe, Germany, Jul 21-26 (2013)*, Poster.
- *Slow Relaxation of Magnetization in Lanthanide Ladder and Layered Hydroxide Structures*, P.I. Girginova, B. Monteiro, C.C.L. Pereira, J. Marçalo, L.C.J. Pereira, J.T. Coutinho, I.C. Santos, M. Almeida, *European Conference on Molecular Magnetism - ECMM 2013, Karlsruhe, Germany, Oct 6-10 (2013)*, Poster.
- *Single-Ion Magnet (SIM) Behavior in Uranium Complexes*, L.C.J. Pereira, M.A. Antunes, J.T. Coutinho, I.C. Santos, H. Bolvin, M. Mazzanti, J. Marçalo, M. Almeida, *European Conference on Molecular Magnetism - ECMM 2013, Karlsruhe, Germany, Oct 6-10 (2013)*, Oral.
- *Uranium(III) Complexes as Single-Ion Magnets – Synthesis and Structural Characterization*, M.A. Antunes, J.T. Coutinho, L.C.J. Pereira, I.C. Santos, H. Bolvin, M. Mazzanti, J. Marçalo, M. Almeida, *2nd Workshop on Strongly Correlated Systems: From Intermetallics to Molecular Materials, Sacavém, Portugal, Nov 11-12 (2013)*, Oral.
- *Magnetic Characterization of U(III) Single-Ion Magnets*, J.T. Coutinho, M.A. Antunes, L.C.J. Pereira, I.C. Santos, H. Bolvin, M. Mazzanti, J. Marçalo, M. Almeida, *2nd Workshop on Strongly Correlated Systems: From Intermetallics to Molecular Materials, Sacavém, Portugal, Nov 11-12 (2013)*, Oral.
- *A Multifunctional Layered Dysprosium Hydroxide, $Dy_8(OH)_{20}Cl_4 \cdot 6H_2O$ – From Slow Relaxation of Magnetization to Gas Sensing*, B. Monteiro, C.C.L. Pereira, J.T. Coutinho, A.J. Moro, J.C. Lima, L.C.J. Pereira, J. Marçalo, M. Almeida, *2nd Workshop on Strongly Correlated Systems: From Intermetallics to Molecular Materials, Sacavém, Portugal, Nov 11-12 (2013)*, Oral.
- *Preparation of Submicron Uranium Carbides for ISOLDE Targets*, M.S. Henriques, A. Cruz, J. Marçalo, T. Stora, A.P. Gonçalves, *2nd Workshop on Strongly Correlated Systems: From Intermetallics to Molecular Materials, Sacavém, Portugal, Nov 11-12 (2013)*, Oral.

EDUCATION

- Member of the Scientific Board and Lecturer on Mass Spectrometry of the Course *Modern Methods of Structure Elucidation–2013*, Centro de Química Estrutural - Instituto Superior Técnico, Lisboa, 11-15 Nov 2013 (<http://cq.e.ist.utl.pt/events/mmse/next.php>).

PROJECTS

- *Portuguese Mass Spectrometry Network – IST/ITN-Node*, FCT - RNEM. Leading Institution: FCUL; J. Marçalo, IST/ITN Coordinator; Jan-Dec 2013.
- *Portuguese Mass Spectrometry Network*, FCT - ROTEIRO/0028/2013. Leading Institution: FCUL; J. Marçalo, Management Team member/Manager of the IST-UL Node; submitted.
- *CATSUS - Catalysis and Sustainability* (Doctoral Programme), FCT - PD/00248/2012. Leading Institution: IST; J. Marçalo, IST Team member; approved/running (<http://catsus.tecnico.ulisboa.pt/>).

SCIENTIFIC COMMITTEES

- Member of the Management Committee of COST Action CM1006 - *EUFEN: European f-Element Network*.

NAME: João Paulo Arriegas Estevão Correia Leal

CATEGORY: Auxiliary Researcher (Habilitation)

IST-ID: 5364

ACTIVITIES

Nº	Activity Description	R&D (%)
1	Catalytic applications of f-element inorganic compounds	20
2	Molecular energetics of organic, inorganic and organometallic compounds	30
3	Degradation and valorisation of bio-recalcitrant compounds and Synthesis of hybrid materials for biomedical applications	10
4	Teaching and Orientation	25
5	Services	15
Total		100

WORK SUMMARY

Nº	Work Summary and Main Achievements
1	<p><i>Nanoparticles and nanostructured compounds for the elimination of gaseous primary pollutants</i></p> <p>The focus of this activity is to obtain f-element containing intermetallic nanoparticle compounds and use them as catalysts for the elimination/valorisation of pollutants as methane, carbon dioxide or nitrous oxide. Some catalysts were synthesized as nanoparticles and results obtained so far show a superior performance when compared with existing commercial ones. New synthetic techniques (spinning deposition) were used to obtain more effective nanoparticles.</p>
2	<p><i>Energetics of diols with alkaline-earth metals, silicon and lanthanides</i></p> <p>Enthalpies of formation of several compounds resulting from the synthesis with diols were determined and the corresponding reactivity and catalytic properties accessed.</p> <p><i>Thermochemical properties databases and properties prediction</i></p> <p>The Therminfo database (http://www.therminfo.com) implemented and developed by a Portuguese team continue to be regularly improved, including in the new release much more compounds and properties. Also new models for properties prediction (both for ionic compounds and covalent organic ones) were developed. These models will be in a very short period implemented in Therminfo database.</p>
3	<p><i>Degradation studies of bio-recalcitrant compounds</i></p> <p>Degradation and valorisation of recalcitrant compounds were studied by using radiation as a tool. Results compiled so far show that radiation can be used both for the degradation of compounds and for the obtainment of new added value ones.</p>

4	<i>Delivering of classes of Química I (Licenciatura Ciências da Saúde) Supervision and Co-supervision of Ph.D. and Master Thesis</i>
5	<i>Representation of Portuguese Chemical Society (SPQ) on the IAVE-MEC. President of the Scientific Council of IAVE-MEC. Member of the Coordination Committee of C²TN.</i>

PUBLICATIONS

Papers

- J. Madureira, R. Melo, M.L. Botelho, J.P. Leal, I.M. Fonseca, Effect of ionizing radiation on antioxidant compounds present in cork wastewater, *Water Science and Technology*, 67, 374-379 (2013), <http://dx.doi.org/10.2166/wst.2012.544>
- C. C. L. Pereira, S. Dias, I. Coutinho, J. P. Leal, L. C. Branco, C. A. T. Laia, Europium(III)tetrakis(β -diketonate) complex as an ionic liquid – a calorimetric and spectroscopic study, *Inorganic Chemistry*, 52, 3755-3764 (2013), <http://dx.doi.org/10.1021/ic3023024>
- L. Teixeira, J. P. Leal, A. O. Falcão, Random Forests for Feature Selection in QSPR Models – an Application for Predicting Standard Enthalpy of Formation of Hydrocarbons, *J. Cheminformatics*, 5:9 (2013), <http://dx.doi.org/10.1186/1758-2946-5-9>
- R. Amadeu, J. P. Leal, Ventajas del uso de simulaciones por ordenador en el aprendizaje de la física, *Enseñanza de las Ciencias*, 31, 177-188 (2013), WOS:000328095300011
- S. C. Leal, J. P. Leal, One example of a chemistry e-lab experiment: chemical equilibrium reaction, *International Journal of Online Engineering*, 9, 44-47 (2013), <http://dx.doi.org/10.3991/ijoe.v9iS8.3380>

Proceedings

- S. C. Leal, J. P. Leal, A new Chemistry e-lab experiment: Chemical equilibrium reaction, *Proceedings 2nd Experiment@ International Conference (exp.at 13)*, ISBN: 978-989-96999-1-5. (2013), Instituto de Educação da UL, nº187.

Other Publications

- L. Teixeira, R. C. Santos, J. P. Leal, A. O. Falcão, J. A. Martinho Simões, ThermInfo: A System for Collecting, Retrieving, and Estimating Reliable Thermochemical Data (2013), [arXiv:1302.0710](https://arxiv.org/abs/1302.0710) (Cornell University Library).
- L. Teixeira, J. P. Leal, A. O. Falcão, Automated Identification and Classification of Stereochemistry: Chirality and Double Bond Stereoisomerism (2013), [arXiv:1303.1724](https://arxiv.org/abs/1303.1724) (Cornell University Library)
- J. P. Leal, Destilação, *WikiCiências*, 2013, 4(1), 764 (2013), <http://wikiciencias.casadasciencias.org/index.php/Destilação>

COMMUNICATIONS

- *O milagre da água*, J.P. Leal, *Externato da Luz, Lisbon, Portugal, Feb (2013)*, Invited Talk.
- *Can coordination compounds be considered ionic from the energetic point of view?*, J.P. Leal, *11º Encontro Nacional de Química-Física*, Porto, Portugal, May (2013), Invited Talk.
- *Materiais didáctico-pedagógicos no ensino da química*, S.C. Leal, J.P. Leal, *I Encontro Internacional da Casa das Ciências*, Lisbon, Portugal, Mar (2013), Oral Communication.
- *Poderá a internet fomentar um novo tipo de iliteracia*, J.P. Leal, *I Encontro Internacional da Casa das Ciências*, Lisbon, Portugal, Mar (2013), Oral Communication.
- *Cativar para a Química: desafios e soluções*, M.M. Varela, J. P. Leal, *I Encontro Internacional da Casa das Ciências*, Lisbon, Portugal, Mar (2013), Oral Communication.
- *A new Chemistry e-lab experiment: Chemical equilibrium reaction*, S.C. Leal, J.P. Leal, *2nd Experiment@ International Conference (exp.at 13)*, Coimbra, Portugal, Sep (2013), Oral Communication.
- *O e-lab e o ensino experimental de química no ensino básico e secundário*, S.C. Leal, J. P. Leal, *I Encontro Internacional da Casa das Ciências*, Lisbon, Portugal, Mar (2013), Poster Communication.

- *Gas phase affinity scales for ions typical of ionic liquids*, J. Vitorino, J.P. Leal, M.E. Minas da Piedade, *5th International Congress on Ionic Liquids (COIL-5)*, Vilamoura, Portugal, Apr (2013), Poster communication.
- *Acid-basic proprieties of calcium-f element bimetallic oxide nanocatalysts*, A.C. Ferreira, J. P. Leal, J. B. Branco, *2nd European f-Element Network*, Dublin, Ireland, Apr (2013), Poster communication.
- *Nanomaterials with f block elements: influence of chemical/physical properties in catalytic performance*, A.C. Ferreira, J.P. Leal, J.B. Branco, *11º Encontro Nacional de Química-Física*, Porto, Portugal, May (2013), Poster communication.
- *Experiência e-lab: equilíbrio químico para o ensino da Química*, S.C. Leal, J. P. Leal, H. Fernandes, *XXIII Encontro Nacional da SPQ*, Aveiro, Portugal, Jun (2013), Poster Communication.
- *Ln(III) tetrakis(β -diketonate) complexes (Ln(III) = Dy, Gd, Tb) as multifunctional ionic liquids*, B. Monteiro, L.C.J. Pereira, I. Coutinho, J.P. Leal, J. Marçalo, C.A.T. Laia, C.C.L. Pereira, *XXIII Encontro Nacional da SPQ*, Aveiro, Portugal, Jun (2013), Poster Communication.
- *Can a simple model be used to estimate solid compounds enthalpies of formation?*, J. P. Leal, *CQB-day*, Lisbon, Portugal, Jul (2013), Poster Communication.
- *Improving QSPR Models for Predicting Standard Enthalpy of Formation with a Hybrid Approach for Feature Selection*, A.L. Teixeira, J.P. Leal, A.O. Falcão, *CQB-day*, Lisbon, Portugal, Jul (2013), Poster Communication.
- *Um laboratório remoto no ensino da Química*, S.C. Leal, J.P. Leal, H. Fernandes, *VIII Conferência Internacional de TIC na Educação – Challenges 2013*, Braga, Portugal, Jul (2013), Poster Communication
- *Nanocatalysts with f block elements to syngas or hydrocarbons*, A.C. Ferreira, J.P. Leal, J. B. Branco, *EUROPACAT XI*, Lyon, France, Sep (2013), Poster Communication.

EDUCATION

Theses Supervision

- Supervisor, Ph.D. Thesis, *Novas tecnologias da informação e comunicação e trabalho laboratorial: desmistificação de factores de insucesso e produção de materiais didáctico/pedagógicos*, by Sérgio Carreira Leal, 4thYear (FCT grant–SFRH/BD/44889/2008) (FCUL/IST-ITN).
- Supervisor, Ph.D. Thesis, *O Ensino da Química no Século XXI: as novas tecnologias ao serviço da Química*, by Maria Manuela Lameiras Varela, 4thYear (FCUL/IST-ITN).
- Co-supervisor (with A. Falcão, FCUL), Ph.D. Thesis, *ThermInfo: Técnicas de Data-Mining para Previsão de Propriedades Termoquímicas*, by Ana Isabel Lino Teixeira, 3th Year (FCT grant–SFRH/BD/69942/2010-2014) (FCUL/IST-ITN).
- Co-supervisor (with J. Marçalo, IST-ITN and J.K. Gibson, Lawrence Berkeley Natl Lab), Ph.D. Thesis, *Exploring the chemical properties of elementary actinide species in the gas phase*, by Ana Filipa Folgado de Lucena, 3rd Year (FCT grant–SFRH/BD/69942/2010-2014) (FCUL/IST-ITN).
- Co-supervisor (with J.B. Branco, IST/ITN), Ph.D. Thesis, *Nanopartículas de Compostos Intermetálicos para a Eliminação Catalítica de Poluentes Primários*, by Ana Cristina Gomes Ferreira, 3rdYear (FCT grant–SFRH/BD/69942/2010) (FCUL/IST-ITN).
- Supervisor, Master Thesis, *Evolução temporal do conceito de Elemento em Química*, by Paula Maria Mendes Bandarra das Neves, concluded Dec 2013 (FCUL).

Teaching

- Theoretical-practical and laboratory classes of “Química I” (Licenciatura de Ciências da Saúde), FCUL.

Jury Membership

- Examiner in the Ph.D Jury of “Estudo Termoquímico Experimental e Computacional de Derivados da Pirimidina” by Tiago Luis Pereira Galvão, Faculdade de Ciências, Universidade do Porto, Dec 2013.

- Examiner in the Master Thesis Jury of “Simulação computacional das leis do movimento no ensino secundário” by Solange de Oliveira Palavras, Faculdade de Engenharia e Ciências Naturais, Universidade Lusófona de Humanidades e Tecnologias, Jul 2013.

Other

- Contributor of WikiCiências/Casa das Ciências project, <http://wikiciencias.casadasciencias.org/>.

PROJECTS

Running

- *Estudo cinético da degradação de compostos biorecalcitrantes por radiólise pulsada (PTDC/QUI-QUI/104229/2008), (2010-2013). Leading Institution: IST/ITN. Team member: J.P. Leal (15%).*
- *Materiais híbridos para aplicações biomédicas (PTDC/CTM/101115/2008), (2010-2013). Leading Institution: U. Aveiro. Team member: J. P. Leal (5%).*
Application of Ionizing Radiation for a Sustainable Environment (RECI/AAG-TEC/0400/2012) (2013-2015). Leading Institution: IST/ITN. Team member: J. P. Leal (15%).

SCIENTIFIC COMMITTEES

- Representation of Portuguese Chemical Society (Sociedade Portuguesa de Química - SPQ) at Conselho Científico do Instituto de Avaliação Educativa (IAVE) of Ministério da Educação e Ciência (MEC).
- Foi eleito presidente desse Conselho pelos pares das restantes Sociedades Científicas.
- Member of the Editorial Board of E-Journal of Chemistry (<http://www.hindawi.com/journals/chem/>).

SCIENTIFIC VISITORS

- J.M. Vitorino, Centro de Química e Bioquímica, FCUL, several periods, Synthesis and characterization of Ionic Liquids.

Name: Joaquim Miguel Badalo Branco

Category: Auxiliary Researcher

IST-ID: 5366

ACTIVITIES

Nº	Activities Description	R&D (%)
1	Scientific and technical activities	75
2	Training and teaching activities	20
3	Services and managing activities	5
Total		100

WORK SUMMARY

Nº	Work Summary and Main Achievements
1	The 2013 activities include: (A) the synthesis, characterization and reactivity studies of intermetallic compounds containing actinides and lanthanides nanocatalysts (Ana Cristina Gomes Ferreira Ph.D. thesis) and (B) initial steps for the development of a high pressure continuous reactor (type flow reactor) for methane and carbon dioxide activation studies aiming the production of alcohols (Cybelle Soares, Research Grant). For the first time, nanoparticles of M-f block elements (e.g. LaNi ₅) intermetallic compounds were obtained and properly characterized. To our knowledge, this is the first time that suitably results were obtained in this research field. Their chemical properties continued to

	<p>be evaluated by heterogeneous catalytic studies of important environmental issues such as the activation and valorisation of CH₄ and CO₂ as valuable C1 feedstocks and N₂O as oxidant either for the production of syngas or C2 hydrocarbons over f block elements based nanocatalysts.</p> <p>The development of a high pressure continuous reactor (type flow reactor) for methane and carbon dioxide activation studies aiming the production of alcohols started and the synthesis of nanoparticles of Cu-f block elements intermetallic compounds (Ce, Th, U) using an electrospinning technique undertaken. The expected high surface areas will bring benefits to the catalytic properties of these materials aiming the production of alcohols.</p> <p>The results shown that nanoparticles of IC containing f-block elements (e.g. LaNi₅, LaCu₂, SmCo₅ and DyFe₃) can be successfully produced by electrospinning. To our knowledge this is the first time that IC nanoparticles were successfully obtained by this method.</p> <p>Collaborations continued with other research groups within and outside CTN in different areas. Of note is the continued collaboration with the CTN/UFA-Nuclear Instruments Laboratory Group in the field of low temperature gas discharges and its applications to the activation of CH₄ and CO₂.</p>
2	A significant part of the activity was the training of research students, namely, a Ph.D. and a research grant (FCT, BI) student. The financial support for the work was from FCT, via research projects.
3	A minor part of the activity was dedicated to support and maintenance of UCQR elemental analysis infrastructure and QIO nitrogen filled glove boxes. Managing activities as head of the QIO Catalysis and Catalysts Synthesis and Characterization laboratories continued as well.

PUBLICATIONS

- M.R. Gonçalves, A. Gomes, J. Condeco, T.R.C. Fernandes, T. Pardal, C.A.C. Sequeira, J.B. Branco, *Electrochemical conversion of CO₂ to C₂ hydrocarbons using different ex situ copper electrodeposits*, *Electrochimica Acta* 388–392, 102 (2013). (<http://dx.doi.org/10.1016/j.electacta.2013.04.015>)

COMMUNICATIONS

- Ana C. Ferreira, J.P.Leal, Joaquim B. Branco, “*Acid-basic proprieties of calcium-f element bimetallic oxide nanocatalysts*”, COST Action CM1006 – EUFEN 2, Dublin, Abril 2013.
- Ana C. Ferreira, J.P.Leal, Joaquim B. Branco, “*Nanomaterials with f block elements: Influence of chemical/physical properties in catalytic performance*”, 11º Encontro de Química-Física, Porto, May 2013.
- Ana C. Ferreira, J.P.Leal, J. B. Branco, “*Nanocatalysts with f block elements*” EuropaCat XI, Lyon, September de 2013.)

EDUCATION

- Co-supervisor, Ph.D Thesis, *Nanopartículas de Compostos Intermetálicos para a Eliminação Catalítica de Poluentes Primários*, by Ana Cristina Gomes Ferreira, 3rd Year (FCT grant–SFRH/BD/69942/2010-2014) (FCUL/IST-ITN).
- Supervisor, Research Grant, *Mitigação do CO₂ e produção de metanol através do “reforming” do CH₄*, by Cybelle Soares (PTDC/AAG-TEC/3324/2012, (2013-2015).

PROJECTS

- Responsible; *CO₂ mitigation and production of methanol by reforming of CH₄*, PTDC/AAG-TEC/3324/2012, IST/ITN Coordinator; Joaquim Branco (35%); FCUL partner; Funding 2013 (25839,00 Euros).
- Team member, *Increasing the energy efficiency of plasma conversion of methane*, PTDC/FIS-PLA/2135/2012, IST/IPFN Coordinator, Nuno Pinhão, Joaquim Branco (15%), ISEL partner; Funding 2013 (15407,04 Euros).

- Team member; *Application of Ionizing Radiation for a Sustainable Environment*, RECI/AAG-TEC/0400/2012, IST/ITN Coordinator Luisa Botelho; Joaquim Branco (15%), Funding 2013 (74920, 35 Euros).
- Responsible; *Implementação do processo de extração catalítica para o tratamento químico de resíduos sólidos orgânicos: plásticos não conformes e resíduos orgânicos* (IMPEC-TRESOR), Sociedade Ponto Verde, IST/ITN, Coordinator (50%), under evaluation (514854 Euros).

PATENTS

- “Selective electrochemical conversion of CO₂ into C₂ hydrocarbons”; Proponent: OMNIDEA; Inventores: T. Pardal, R. Fernandes, M. Gonçalves, J. Condeço, A. Boavida, J. Branco; international ambit (INPI, Pt 105566 de 2011). International-European Patent (classification C25B 3/04 (2006.01); Patent n^o: 12715237.9-1360 PCT/PT2012000008) (21.10.2013)

NAME: José Manuel da Cunha Oliveira Figueira Carretas

CATEGORY: Auxiliary Researcher

IST-ID: 5369

ACTIVITIES

N ^o	Activity Description	R&D (%)
1	Mass Spectrometry Studies of the Coordination Chemistry of Lanthanides and Actinides	70
2	Samarium Complexes with Diamino Bis(phenolate) Ligands	30
Total		100

WORK SUMMARY

N ^o	Work Summary and Main Achievements
1	We have been using electrospray ionization quadrupole ion trap mass spectrometry (ESI-QIT/MS) to investigate fundamental gas-phase properties of the lanthanides and actinides. ESI-QIT/MS was used to explore O ₂ -addition to uranyl(V) species. Gas-phase reactions of the mononegative ions [UO ₂ X ₂] ⁻ (X = NO ₃ , HCOO, CH ₃ COO, CF ₃ COO, CH ₃ COS, F, Cl, Br, I, OH, NCS) with the background O ₂ present in the QIT yielded [UO ₂ (O ₂)X ₂] ⁻ ions. Dioxygen addition resulted in superoxo complexes and formally corresponds to the oxidation of U(V) to U(VI) [U ^V O ₂ X ₂] ⁻ + O ₂ → [U ^{VI} O ₂ (O ₂)X ₂] ⁻ . The measured oxidation rates for the [UO ₂ X ₂] ⁻ ions were diverse, ranging from the substantially fast [UO ₂ (OH) ₂] ⁻ (16.3 s ⁻¹) to the slow [UO ₂ I ₂] ⁻ (0.15 s ⁻¹). DFT studies of the structures and energetics of selected species have elucidated the experimental observations.
2	Samarium complexes supported by the diamine bis(phenol) proligand H ₂ (^t Bu ² O ₂ NN ⁺) = Me ₂ N(CH ₂) ₂ -N{CH ₂ -(2-OH-3,5- ^t Bu ₂ -C ₆ H ₂) ₂ } were prepared and structurally characterized. [Sm(^t Bu ² O ₂ NN ⁺) ₂](μ-Cl) ₂ (1) was obtained from reaction of SmCl ₃ with K ₂ (^t Bu ² O ₂ NN ⁺) in THF, DME or pyridine. The reaction of 1 with LiNEt ₂ gave a zwitterionic bimetallic complex of Sm and Li, [Sm(^t Bu ² O ₂ NN ⁺) ₂ Li] that formed upon ligand redistribution and did not allow the isolation of the expected diethylamido derivative. Analogously treatment of Sm{N(SiMe ₃) ₂ } ₃ with H ₂ ^t Bu ² O ₂ NN ⁺ led to a zwitterionic samarium complex [Sm(^t Bu ² O ₂ NN ⁺)(^t Bu ² O ₂ N(H)N ⁺)] that also displays a 2ligand:1Sm ratio. In this complex the samarium is formally an ate centre and the tripodal nitrogen of one of the ligands is protonated. The reaction of 1 with Li[2-(CH ₂ NMe ₂)C ₆ H ₄] proceeded through chloride metathesis to give [Sm(^t Bu ² O ₂ NN ⁺)(k ² -{2-(CH ₂ NMe ₂)-C ₆ H ₄ })].

PUBLICATIONS

- E. Mora, L. Maria, B. Biswas, C. Camp, I.C. Santos, J. Pécaut, A. Cruz, J.M. Carretas, J. Marçalo, M. Mazzanti, Diamine bis(phenolate) as supporting ligands in organoactinide(IV) chemistry.

Synthesis, structural characterization, and reactivity of stable dialkyl derivatives, *Organometallics*, 32, 1409-1422 (2013), dx.doi.org/10.1021/om3010806.

- J.M. Carretas, S. Barroso, J. Cui, A. Cruz, I. C. Santos, A.M. Martins, Diamine bis(phenolate) samarium complexes: syntheses and structures, *Inorganica Chimica Acta*, 407, 175-180 (2013), dx.doi.org/10.1016/j.ica.2013.07.051.
- J. M. Carretas, J. Cui, A. Cruz, I.C. Santos, J. Marçalo, Crystal structure of bis[1-{(3,5-dimethyl-1H-pyrazol-1-yl)methyl}-3,5-dimethyl-1H-pyrazol-2-ium] hexachloridouranate(IV) – [H₂C(3,5-Me₂pz)(3,5-Me₂pzH)]₂[UCl₆], *Journal of Structural Chemistry*, accepted for publication.
- J. Cui, I.C. Santos, J.M. Carretas, Yttrium and samarium complexes with a linked 1,4,7-triazacyclononane-aryloxide ancillary ligand, *Journal of Structural Chemistry*, accepted for publication.

COMMUNICATIONS

- *Oxygen Addition Reactions of Uranyl(V) Complexes in the Gas Phase*, A.F. Lucena, J.M. Carretas, Y. Gong, M.C. Michelini, J.K. Gibson, J. Marçalo, *2nd Meeting of the European f-Element Network (EUFEN-2), Dublin, Ireland, Apr17-18 (2013), Poster presentation.*

Name: Maria Teresa Oliveira de Almeida Gasche

Category: Auxiliary Researcher

IST-ID: 5376

ACTIVITIES

Nº	Activity Description	R&D (%)
1	Scientific and technical activities	75
2	Training and teaching activities	20
3	Services activities	5
Total		100

WORK SUMMARY

Nº	Work Summary and Main Achievements
1	<p>Studies concerning important environmental issues such as the activation and valorization of methane and carbon dioxide as valuable C1 feedstock's, namely through the catalytic partial oxidation of CH₄ (POM reaction) using N₂O as oxidant were continued.</p> <p>Research concerning the synthesis of binary intermetallic compounds (IC) nanoparticles containing, f-block elements were performed. Nickel lanthanide and actinide nanoparticles catalysts were obtained by sol-gel method. Electrospinning technique was also used as new method in order to obtain nanoparticles.</p> <p>The catalytic activity and stability to produce synthesis gas through partial oxidation of methane (POM) of these compounds were studied. They were very active and selective for the partial oxidation of methane and synthesis gas production. Other systems containing other d-elements and f-block elements were studied. The characterization of nanoparticles was done with (SEM), (XRD), elemental analysis and (TEM).</p> <p>Studies concerning CO₂ mitigation and production of methanol by reforming of CH₄ were started. Synthesis of some binary intermetallic compounds of the type (AnM_x=2-6, An = Ce, Eu, Yb, Th and M = Fe, Co, Cu) were performed. Already some catalytic studies were done.</p> <p>The importance of ionic liquids research is increasing and the demand of reliable thermodynamic or physical data of pure components and mixtures increases. Our research concerning ionic liquids (ILs) properties continued. Viscosity and density measurements of pure ILs and mixtures were done.</p>
	The training and teaching activities concerns the work performed with research students,

2	namely, a Ph.D. student and a research student. The financial support for the work related to these two students was mostly from FCT, via research projects.
3	The services to the community consisted in the organization of internal seminars in the research group.

PROJECTS

- *Team member (50%): "CO₂ mitigation and production of methanol by reforming of CH₄", PTDC/AAG-TEC/3324/2012, IST/ITN Coordinator; Joaquim Branco (35%); FCUL partner, recommended for funding (172260 Euros), started in September 2013.*

NAME: Leonor Maria de Jesus Maria

CATEGORY: Auxiliary Researcher (Ciência 2008)

IST-ID: 4833

ACTIVITIES

Nº	Activity Description	R&D (%)
1	Uranium complexes supported by a bis(phenolate) cyclam ligand	35
2	Local scientific coordination of the project " <i>Chiral metalla-diaminocarbene precatalysts for asymmetric catalytic reactions obtained by the metal-mediated approach</i> " (PTDC/QUI-QUI/114139/2009): Synthesis of lanthanide complexes	30
3	Gas-phase chemistry of actinides with biomolecules	15
4	Supervision and training of the graduate student Marina Soares	5
5	Management of the Organometallic Chemistry Laboratory	10
6	Preparation of proposals for the IFCT and post-doc calls	5
Total		100

WORK SUMMARY

Nº	Work Summary and Main Achievements
1	<p>The reactivity studies of the trivalent uranium complex $[U^{III}\{(t^{Bu}O)_2ArO\}_2Me_2\text{-cyclam}]$, anchored on a dianionic bis(phenolate) tetraazamacrocyclic ligand, with redox-active substrates were continued. This bulky ligand allowed to the stabilization of uranium complexes on the oxidation state +3, +4, +5 and +6. The reduction of an azobenzene molecule by the uranium(III) complex leads to the isolation of the uranium(VI) trans-bis(imido) complex, $[U^{VI}\{(t^{Bu}O)_2ArO\}_2Me_2\text{-cyclam}\}(=NPh)_2]$. The X-ray diffraction analysis showed that the U=N imido bond distances are short, in agreement with a multiple uranium–nitrogen bonding. The characterization of this new complex by ¹H NMR and IR spectroscopy also corroborated the formation of the bis(imido) uranium(VI) complex. The X-ray diffraction analyses were done in collaboration with Dr. Isabel C. Santos (Solid State Group).</p>
2	<p>Within the project PTDC/QUI-QUI/109846/2009, the synthetic studies were continued with the aim of finding an adequate ligand system for isolating lanthanide aminocarbene complexes. The coordination abilities of the bis(phenolate) cyclam based ligands, $[(R^2ArO)_2Me_2\text{-cyclam}]^{2-}$, toward Yb(II) and Sm(II) were pursued in order to isolate new well defined lanthanide platforms.</p> <p>The reactions with the new ligand $K_2[(Ar^{Me_2}O)_2Me_2\text{-cyclam}]$ and $YbI_2(THF)_2$ have led to the formation of dinuclear and trinuclear Yb(II) species $[Yb\{(Ar^{Me_2}O)_2Me_2\text{-cyclam}\}YbI_2(THF)_2]$ and $[Yb\{(Ar^{Me_2}O)_2Me_2\text{-cyclam}\}YbIYb\{(Ar^{Me_2}O)_2Me_2\text{-cyclam}\}]I$, respectively. Single crystal X-ray diffraction analysis structures show YbO_2Yb moieties that are bridged by phenolate oxygen atoms.</p> <p>The synthesis of the divalent samarium complex $[Sm\{(Ar^{Me_2}O)_2Me_2\text{-cyclam}\}]$ was optimized and preliminary cyclic voltammetry studies, in order to evaluate the redox behaviour, were started in collaboration with Elisabete Alegria (ISEL). Reactivity studies of this new</p>

	<p>complex toward unsaturated substrates and inorganic redox active substrate were initiated. The characterization and formation of the lanthanide complexes were followed by NMR spectroscopy and by mass spectrometry (ESI-MS).</p> <p>This work was partially developed by the graduate student Marina Soares under my supervision and the single crystal X-ray diffraction analysis was performed in collaboration with Dr. Isabel C. Santos (Solid State Group).</p>
3	<p>ESI-QIT/MS was used to produce gas-phase complexes of neutral and deprotonated glycine with actinyl ions, $U^{VI}O_2^{2+}$ and $An^VO_2^+$ ($An = {}^{238}U, {}^{237}Np, {}^{242}Pu$). Complexes $[UO_2(X)(Gly)_2]^+$ and $[UO_2(X)_n(Gly-H)_{3-n}]^-$ ($X = (Gly-H)^-, Cl^-, NO_3^-, n = 0, 1, 2$) were produced. The CID of the isolated complexes yielded several fragments mainly by HX loss, ligand loss and decarboxylation steps; rapid reaction with the background water was also observed.</p> <p>Uranyl complexes with neutral and deprotonated α-amino acids, with different side chain functional groups (aspartic acid, histidine and cysteine), were also produced by electrospray ionization of solutions of uranyl(VI) and mixtures of two amino acids in a 1:1 ratio: $[UO_2(aa^1)_2(aa^2-H)]^+$ or $[UO_2(aa^1)(aa^1-H)(aa^2)]^+$, $[UO_2X(aa^1-H)(aa^2-H)]^-$, and $[UO_2(aa^1-H)_2(aa^2-H)]^-$ ($X = Cl^-, NO_3^-$). Collision induction dissociation (CID) of the mixed-ligand species primarily showed loss of a neutral aa, followed by reaction with the water for some of the products. In the positive mode, competitive CID and hydrolysis seem to indicate that the strength of the (neutral aa)-UO_2^{2+} interaction follows the order His>Asp>Cys. Preliminary studies of the coordination of nucleobases towards uranyl ions in gas-phase and competitive CID studies were also initiated in the year 2013.</p> <p>This work was developed in collaboration with Dr. Joaquim Marçalo, Dr. John Gibson and with the PhD student Ana F. Lucena.</p>
4	Supervision of the graduate student Marina Soares within the research activities described in 2. Marina Soares started the experimental work for M.Sc Thesis in September 2013 under my supervision, in collaboration with Elisabete Alegria from Instituto Superior de Engenharia de Lisboa
5	<p>The management of the Organometallic synthesis laboratory includes the purchase of reagents and solvents and the detection and supervision of all needs concerning repair of the equipment and facilities.</p> <p>In addition, during 2013 several problems were detected with the nitrogen filled glovebox of the Laboratory of organometallic synthesis, and some part of my time was dedicated to solving these problems, in order to get an adequate inert atmosphere to manipulate air-sensitive compounds.</p>
6	Proposal to the last call for Investigator FCT, entitled "Greenhouse gases activation and transformation: an organo-f-element approach" was prepared and a proposal for the last FCT call for a post-doctoral fellowship entitled "Gas-phase molecular transformations for the synthesis of new f-element species" was prepared and refused for funding.

PUBLICATIONS

- E. Mora, L. Maria, B. Biswas, C. Camp, I. C. Santos, J. Pécaut, A. Cruz, J. M. Carretas, J. Marçalo, M. Mazzanti, Diamine Bis(phenolate) as Supporting Ligands in Organoactinide(IV) Chemistry. Synthesis, Structural Characterization and Reactivity of Stable Dialkyl Derivatives, *Organometallics*, 2013, 32, 1409–1422. DOI: [10.1021/om3010806](https://doi.org/10.1021/om3010806).
- L. Maria, I. C. Santos, L. G. Alves, J. Marçalo, A. M. Martins, Rare Earth Metal Complexes Anchored on a New Dianionic Bis(phenolate)dimethylamine-Cyclam Ligand, *J. Organomet. Chem.*, 2013, 728, 57-67. DOI: [10.1016/j.jorganchem.2012.12.026](https://doi.org/10.1016/j.jorganchem.2012.12.026).
- C. Fernandes, L. Maria, L. Gano, I. C. Santos, I. Santos, A. Paulo, Re(I) and $99mTc(I)$ tricarbonyl complexes with ether-containing pyrazolyl-based chelators: Chemistry, biodistribution and metabolism, *J. Organomet. Chem.*, Publication Date (Web): November 21, 2013. DOI: [10.1016/j.jorganchem.2013.11.013](https://doi.org/10.1016/j.jorganchem.2013.11.013).

COMMUNICATIONS

- *Uranium Complexes Supported by Bis-phenolate Tetraazacyclotetradecane: Insight into the Reactivity of a New Uranium(III) Compound*, Leonor Maria, Isabel C. Cordeiro, Adelaide Cruz, Joaquim Marçalo, Meeting of COST ACTION CM1006 , *European f-Element Network (EUFEN2)*, Dublin, Ireland, April 17th and 18th 2013- Poster.
- *Formation and Dissociation of Uranyl-, Neptunyl- and Plutonyl-Glycine-Complexes in the Gas Phase*, Ana F. Lucena, Leonor Maria, Yu Gong, John K. Gibson, Joaquim Marçalo: Meeting of COST ACTION CM1006 , *European f-Element Network (EUFEN2)*, Dublin, Ireland, April 17th and 18th 2013- Poster.
- *Divalent lanthanide complexes supported by bis(phenolate) cyclam ligands*, L. Maria, E. Mora, V. Sousa, I. C. Santos, K. V. Luzyanin, J. Marçalo, 20th EuCheMS Conference on Organometallic Chemistry(EUCOM XX), St. Andrews, Scotland, June 30th to July 4th - Poster and oral flash presentation.

EDUCATION

- Supervision: Marina Pedro Soares; BI grant under the project PTDC/QUI-QUI/109846/2009 and M.Sc Thesis in preparation with the co-supervision of Elisabete Alegria (ISEL), since September 2013. M.Sc Program in Chemical and Biological Engineering at ISEL.
- Member of the Organizing Committee and tutor of the *School on Modern Methods of Structure Elucidation–2013*, Centro de Química Estrutural – Instituto Superior Técnico (in Collaboration with C2TN), UT, Lisbon, 11-15th November 2013 (<http://cqe.ist.utl.pt/events/mmse/next.php>).

PROJECTS

- *Chiral metalla-diaminocarbene precatalysts for asymmetric catalytic reactions obtained by the metal-mediated approach*, PTDC/QUI-QUI/109846/2009 (April 2011-September 2014), Leading Institution: Centro de Química Estrutural, Instituto Superior Técnico. Local Coordinator and Principal Investigator since March 2013 (25 %). Collaboration with Dr. Konstantin Luzyanin (Dept. Chemistry, Univ. Liverpool, UK; St. Petersburg State University, Russian).
- *From drug design to new materials: structural approach in emergent fields*, RECI/QEQ-QIN/0189/2012), Leading Institution: Centro de Química Estrutural (M. Teresa Duarte), Instituto Superior Técnico. Member of the team (15 %).
- COST ACTION CM1006 - EUFEN: European F-Element Network, participant.

SCIENTIFIC COMMITTEES

- Reviewer of manuscripts submitted to the scientific journals: *Organometallics* and *European Journal of Inorganic Chemistry*.