# Inorganic and Organometallic Chemistry

*Joaquim Marçalo*

The activities of the Group encompass the synthesis, characterisation and reactivity studies of inorganic, organometallic and intermetallic compounds of the actinides and lanthanides. The main goals of the work are to understand the influence of the electronic structure and the size of the f-elements in the properties of their compounds, and to find new applications for these elements. Chemical properties are assessed by stoichiometric reactions and by homogeneous and heterogeneous catalytic studies. Gas-phase ion chemistry and energetics studies, using advanced mass spectrometric and calorimetric techniques, are also undertaken with the same goal.

Important facilities maintained by the Group are a laboratory for catalytic studies, a laboratory for handling the more radioactive actinides, a laboratory for calorimetric studies and thermal analysis, and two select mass spectrometers, a FTICR instrument, with EI and LDI sources, and a QIT instrument, with ESI and APCI sources. The QIT mass spectrometer is part of the National Mass Spectrometry Network (RNEM).

We continued to study important environmental issues such as the activation and valorisation of methane as C1 feedstock, namely through the catalytic partial oxidation of $CH_4$ (POM reaction) using $O_2$ or $N_2O$ as oxidant. The lanthanide and actinide catalysts were obtained by three routes: i) an intermetallic route, ii) a sol – gel route and iii) a molten salt route. Under $O_2$, the molten salt approach allowed the production of hydrocarbons, particularly C3, with an unusual high selectivity (>70%). Under $N_2O$, the main products were C2 hydrocarbons and the increase of the $CH_4/N_2O$ molar ratio had a significant influence on the selectivity. The selective catalytic reduction of $N_2O$ by $CH_4$ is not only as an effective method of $N_2O$ abatement but, in particular, an effective method of $N_2O$ and $CH_4$ valorisation. To our knowledge, this is the first time that such results are reported over molten salts and bimetallic lanthanide or actinide oxides.

The investigation of the coordination chemistry of actinides and lanthanides with O- and N-donor ligands continued. The multidentate aminophenolate ligands $\{(Ar^tBu_2O)_2\text{-cyclam}\}$ and $\{\text{Salan-}^tBu_2\}$ were successively used in the preparation of new Ln(III), U(III) and An(IV) (An = Th, U) complexes with varied structural features.

Gas-phase chemistry/mass spectrometry studies expanded in 2010. New uranium species, namely, the sulfur analogue of uranyl and several uranium carbide cluster ions were produced. The complexation of heterocyclic N-donor bases (building blocks of ligands used in Ln/An separations) towards Ln(III) and An(III) ions was investigated. Key d-transition metal species involved in catalytic processes, namely, Re and Mo complexes, and Ta oxides, were also studied.

Molecular energetics studies continued. An affinity scale of cations commonly used in ionic liquids started to be determined using the $NTf_2$ anion as a reference. The gas-phase acidity of chromanol was determined, on the way to obtaining the acidity of vitamin-E.

In a collaboration with FCT/UNL, new lanthanide-based luminescent materials were prepared using compounds of the type $Ln_8(OH)_{20}Cl_4{\cdot}nH_2O$ as intercalators.

Collaborations continued with the Radiation Technologies: Processes and Products Group (Physics and Accelerators Unit) in the study of gamma-radiation effects on recalcitrant effluents, and with OMNIDEA, Lda., a start-up company devoted to R&D of aerospace technology and energy systems.

Joint projects with the Research Unit "Glass and Ceramic for the Arts" (a collaboration between ITN, FBAUL and FCT/UNL) on lanthanide-containing glasses and ruby glass were pursued.

A relevant part of the activity of the Group is the training of research students, which had a significant increase in 2010. Some of the Group members continue to be involved in undergraduate and post-graduate university teaching. The financial support for the work is mainly from FCT, via research projects and PhD and Post-doc grants. A new project within ACTINET-I3, in Ln/An separation chemistry, was initiated in 2010.

## Research Team

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# f- Block Elements as Catalysts

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## Objectives

The main objectives of this research are: (i) to study the f-block elements behaviour as catalysts or catalytic precursors, (ii) to develop new methods for the preparation of 4f and 5f nanostructured materials for catalytic purposes and (iii) to contribute to the resolution of key environmental issues.

## Introduction

We continue to study the activation and valorisation of methane and carbon dioxide as valuable C1 feedstock's, namely through the catalytic partial oxidation of $CH_4$ (POM reaction) using $O_2$ or $N_2O$ as oxidant. The catalysts were obtained by three routes: i) an intermetallic route, using $LnCu_2$ and $LnNi_2$ (Ln = from La to Yb) or $AnNi_2$ (An = Th, U) and $ThCu_2$ as bimetallic oxides precursors, ii) a sol – gel route (urea or citric acid methods) to obtain nanoparticles of bimetallic oxides and, recently, iii) a molten salt route using eutectic potassium - lanthanide chlorides molten salts. The catalytic reactions were followed on-line by gas chromatography.

## Results

The intermetallic and sol – gel routes allowed the production of syngas with the appropriate $H_2$/CO mol ratio and high conversion of methane over the bimetallic nickel based oxide catalysts, which are cheaper materials with an activity, selectivity and stability comparable to that of the noble metal based catalysts, e.g. 5 wt. % M/$Al_2O_3$ (M = Rh, Pt) (Fig. 1). The good catalytic behaviour of this nickel based catalysts and its high stability is a major achievement since the known and widely studied noble metal based catalysts are limited by their high cost, whereas the deactivation of other catalysts is the major drawback of this reaction that limit a widespread industrial application.

On the other hand, the catalytic performance of the molten salts of the type KCl-LnCl (Ln = La, Ce, Pr, Sm, Gd, Dy, Yb) is clearly different and depends on the rare earth. The main products are now C2 hydrocarbons (except for Ce and Eu) and the best results were those obtained over the lanthanium and samarium catalysts (Sel.C2 ~ 70 %) (Fig. 2). The results obtained for the partial oxidation of $CH_4$ by $N_2O$ confirm this unusual behaviour of the molten salts (Conv. $CH_4$ > 10 %; Sel. C2 ~ 70-80 %). To our knowledge, this is a novelty over molten salts catalysts containing f-block elements.

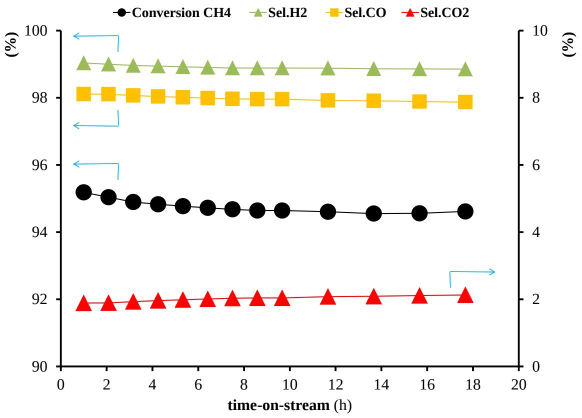

Fig. 1. Bimetallic Ni-U oxide ($2NiO \cdot UO_3$) catalytic activity and selectivity as a function of time on stream at 800 °C for the partial oxidation of methane by $O_2$.

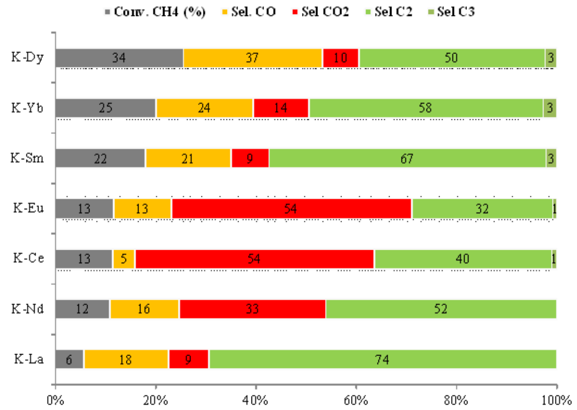

Fig. 2. K-Ln chlorine molten salt catalysts activity and selectivity at 750 °C for the the partial oxidation of methane by $O_2$.

## Published work

A.C. Ferreira, A.M. Ferraria, A.M. Botelho do Rego, A.P. Gonçalves, A.V. Girão, M.R. Correia, T. Almeida Gasche, J.B. Branco, Partial oxidation of methane over bimetallic copper–cerium oxide catalysts, *J. Mol. Catal. A-Chem.* 320 (2010) 47–55.

A.C. Ferreira, A.P. Gonçalves, T. Almeida Gasche, A.M. Ferraria, A.M. Botelho do Rego, M.R. Correia, A.M. Bola, J.B. Branco, Partial oxidation of methane over bimetallic copper- and nickel-actinide oxides (Th, U), *J. Alloys Comp.* 497 (2010) 249–258.

A.C. Ferreira, A.M. Ferraria, A.M. Botelho do Rego, A.P. Gonçalves, M.R. Correia, T. Almeida Gasche, J.B. Branco, Partial oxidation of methane over bimetallic nickel–lanthanide oxides, *J. Alloys Comp.* 489 (2010) 316–323.

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[3] ITN/UCQR, Solid State Group.

## f-Element Chemistry with Multidentate Nitrogen and Oxygen Donor Ligands

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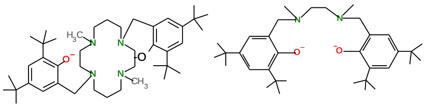
The main goal of this research work is to developed new coordination environments for the f-elements and to synthesize new compounds with potential interest in organic synthesis and catalysis. We continued the investigation of the coordination chemistry of actinides (Th and U) and lanthanides based on O- and N-donor ligands, namely, with the multidentate aminophenolate ligands $L^1$ and $L^2$ (Scheme 1). The reaction of the trans-N,N'-bis(phenolate)-cyclam ligand $L^1$ with $LnCl_3(THF)_x$ (Ln = La, Sm, Yb) and $UI_3(THF)_4$ led to the formation of the neutral compounds $[Ln\{(Ar^tBu_2O)_2\text{-cyclam}\}Cl]$ and $[U\{(Ar^tBu_2O)_2\text{-cyclam}\}I]$ in good yields. The solid-state structures of the La, Sm and U complexes showed that the metal centers are seven coordinated and $L^1$ acts as a hexadentate ligand. The smaller ionic radius of Yb(III) led to the formation of a six-coordinated compound with the macrocycle acting as pentadentate, with one of the nitrogens uncoordinated (Fig.1). The reactions of the tetradentate ligand $L^2$ with $AnCl_4$ (An = Th, U) showed that this bis(aminophenolate) is a good anchor for An(IV) complexes. The new eight coordinated complexes $[An\{Salan\text{-}^tBu_2\}Cl_2L]$ (An = Th, L = dme, bipy; An = U, L = bipy) and $[Th\{Salan\text{-}^tBu_2\}_2]$ were synthesised and characterised by NMR experiments, ESI/QITMS and X-ray diffraction analysis.



$L_1$: $[(Ar^{tBu2}O)_2\text{-cyclam}]^{2-}$

$L_2$: $[Salan\text{-}^tBu2]^{2-}$

Scheme 1

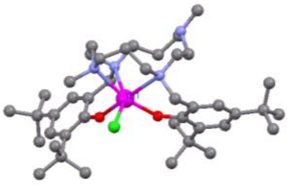


Fig.1 - $[Yb\{(Ar^tBu_2O)_2\text{-cyclam}\}Cl]$

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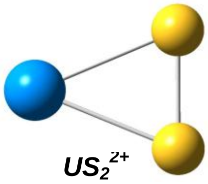
[1] SS Group/UCQR-ITN. [2] Centro de Química Estrutural, IST. [3] INAC, CEA-Grenoble (France).

## Gas-Phase Chemistry and Thermochemistry of Elementary Actinide Molecules

*J. Marçalo, C. C. L. Pereira, A. F. Lucena, A. Pires de Matos, A. P. Gonçalves*[1]*, L. Andrews*[2]*, J. K. Gibson*[3]

Gas-phase chemistry studies, using advanced mass-spectrometry techniques (LDI/FTICRMS and ESI/QITMS), are conducted to search for new elementary actinide species and reactions, and investigate their chemical and thermochemical properties. In 2010, we were able to produce the first synthesis and theoretical description of bare $US_2^{2+}$ (the sulfur analogue of uranyl) in the gas phase. We used FTICRMS to study the reaction of $U^{2+}$ ions with COS in which we observed the sequential, efficient formation of $US^{2+}$ and $US_2^{2+}$. Theoretical studies performed by C.J. Marsden (Univ. Paul Sabatier, Toulouse, France) showed that, in contrast to linear uranyl ($O{=}U^{2+}{=}O$), $US_2^{2+}$ has a strongly bent structure at both B3LYP and CCSD(T) levels of theory, with the linear isomer being some 100 kJ/mol higher in energy. Also in 2010, $UC_n$ and $USi_n$ compounds, obtained by high-temperature synthesis techniques, were investigated by LDI/FTICRMS. $UC_n$ showed to be an efficient precursor for the formation of new $UC_x^+$ and $U_2C_x^+$ (x = 2-14) ions, with $UC_2^+$ being especially abundant; no Si analogues could be obtained from $USi_n$. These LDI studies of $UC_n$ and $USi_n$ samples were accompanied by matrix-isolation spectroscopy experiments with similar samples at the U. Virginia in which new neutral $UC_x$ species could be identified; $USi_n$ is currently under study.



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[1] SS Group/UCQR-ITN. [2] U. Virginia (Chalottesville, VA, USA). [3] Lawrence Berkeley National Lab. (Berkeley, CA, USA).

## Mass Spectrometry Studies of the Coordination Chemistry of Lanthanides and Actinides

*J. Marçalo, C. Lourenço, J. M. Carretas, B. Monteiro, J. P. Leal, I. Paiva*[1]*, L. Berthon*[2]*, J. K. Gibson*[3]

The coordination chemistry of the lanthanides (Ln) and actinides (An) with N-donor ligands is a topic of current interest, as associated to Ln/An separations within advanced nuclear fuel cycles. Some of the ligands used have simple heterocyclic N-donor bases as building blocks. Within the ACTINET-I3/JRP-17 project, we have been using mass spectrometry (ESI/QITMS and LDI/FTICRMS) in the investigation of the complexation properties of different N-donor bases and simple N-donor ligands towards Ln(III) and An(III) ions. The relative affinity of a representative number of N-donor bases towards Ln(III) ions was studied by ESI/QITMS. These experiments indicated that the relative gas-phase affinities of the N-donor molecules followed their gas-phase basicities, with the notable exception of pyridazine for which a $\eta^2$ coordination mode seems to prevail, leading to a stronger bonding. The coordination of the new neutral tetradentate ligand L = bis[3-(2-pyridyl)pyrazolyl]methane (Fig. 1) towards Ln(III) and Y(III) in solution was also studied using ESI/QITMS. Experiments with different M/L ratios as well as CID indicated that the 1:1 stoichiometry was preferred. Comparative studies of the gas-phase affinities of different bases and ligands towards early Ln(III) and Am(III) ions by ESI/QITMS and LDI/FTICRMS are currently under way.

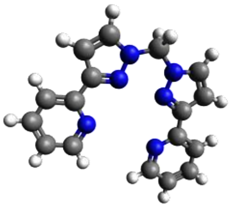

Fig.1 - Bis[3-(2-pyridyl)pyrazolyl]methane

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[1] RRW Group/UPSR-ITN. [2] CEA-Atalante (Marcoule, France). [3] Lawrence Berkeley National Lab. (Berkeley, CA, USA).

## Mass Spectrometry Studies of d-Transition Metal Species

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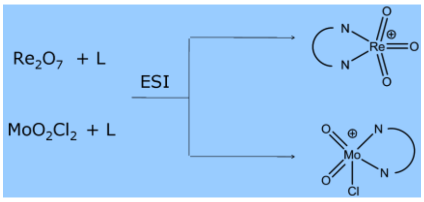
Mass spectrometry can be a useful tool in the study of different aspects of the chemistry of metal compounds. We have been using ESI/QITMS and LDI/FTICRMS in the investigation of key d-transition metal species involved in catalytic processes.



The catalytic activity in olefin epoxidation of $[Re(CH_3)O_3L]$ and $[MoO_2Cl_2L]$ complexes, where L is a bidentate N-donor ligand, is strongly influenced by the electronic and steric nature of L. The relative stability of mono- and bidentate N-donor adducts of $[ReO_3]^+$ and $[MoO_2Cl]^+$ (as models for the neutral complexes) was investigated by ESI/QITMS, to probe the technique as a simple alternative to standard methods (spectrophotometry, NMR) of solution characterization. The results were in overall agreement with spectrophotometric studies of the stability of N-donor adducts of $[Re(CH_3)O_3]$ and $[MoO_2Cl_2]$.

Transition metal oxides have numerous applications as heterogeneous catalysts, support materials, etc., and are present in the reaction centers of many enzymes. To provide fundamental chemical models to rationalize the chemistry in complex multi-charged systems and to obtain new thermodynamic data of ionic and neutral species containing these elements, we have been examining the gas-phase chemistry and thermochemistry of singly and doubly charged transition metal oxide ions by FTICRMS. The ionization energies of TaO and $TaO_2$ have been determined by a bracketing method, employing a selected set of organic compounds of known ionization energies. The oxygen-dissociation energies of singly and doubly charged TaO and $TaO_2$ have also been determined via reactions with several oxidants with different oxygen affinities.

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## Molecular Energetics of Organic, Inorganic and Organometallic Compounds

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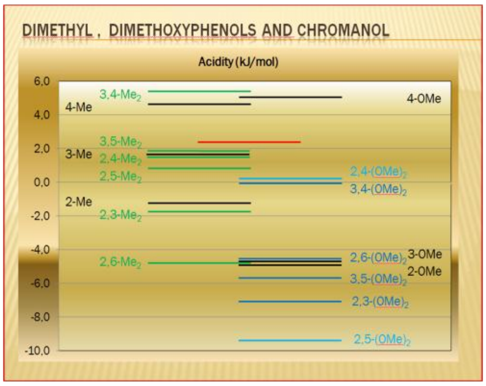
The main objective is to collect energetics data, rationalize it in a systematic way and explore connections between energetics and structure of molecules (both inorganic and organic compounds). Special importance was given to f-element compounds (both on solid state and in solution). To achieve this goal, lanthanide and actinide (organometallic and intermetallic), alkaline and alkaline-earth compounds, hydrocarbons and ionic liquids were studied.

During 2010, an extended version of an already published empirical model for the prediction of the enthalpies of formation of hydrocarbons was enlarged to accommodate CHO compounds. The site www.therminfo.com, online in 2010, allows the retrieving of existing enthalpies of formation (critically analyzed) and the estimation of non existing values for hydrocarbon compounds.

The nature of ionic liquids in the gas phase continued to be studied and the kinetic of some of the reactions where they are involved were investigated using FTICR/MS. The thermal properties of some ionic liquids were studied using thermal analysis techniques and the correspondent reactivity was explored using a QIT/MS apparatus. Also, an affinity scale of cations usually used in ionic liquids formulation started to be determined using the $NTf_2$ anion as a reference.

After conclusion of the gas-phase acidity measurements of di-methoxy and di-methyl-substituted phenols, the gas-phase acidity of chromanol was determined, on the way to obtaining the vitamin-E acidity.



The study of polyalkoxides of alkaline and alkaline-earth metals had new developments: some of the already synthesised compound where calorimetrically measured and the corresponding enthalpies of formation obtained.

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[1] IOC Group/UCQR-ITN & Centro de Química e Bioquímica, FCUL. [2] Centro de Química e Bioquímica, FCUL.

## Decomposition of Recalcitrant Effluents

*J. P. Leal, R. Melo*[1]*, M. L. Botelho*[2]

The degradation/decomposition mechanism of gallic acid was elucidated by using pulse-radiolysis studies to unveil the initial steps and mass spectrometry (ESI-QIT/MS) to identify the major intermediates. New studies are on the way with some other recalcitrant compounds (acetovanilone and sculetol) to see if the decomposition mechanism is similar to the one proposed for gallic acid.

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## Lanthanide-Based Luminescent Materials

*C. C. L. Pereira, B. Monteiro, J. P. Leal, T. Almeida Gasche, L. C. Branco*[1]*, C. A. T. Laia*[1] *, P. Viana Baptista*[2]

The synthesis of new lanthanide-based luminescent materials was pursued. Compounds of the type $Ln_8(OH)_{20}Cl_4{\cdot}nH_2O$ (Ln = Eu, Tb, Dy) were prepared and used as precursors for the synthesis of new materials by intercalation, via chloride ion exchange, of ligands of the beta-diketone and chalcone families and of DNA fragments. The synthesis and characterization of ionic liquids involving anionic Ln complexes (Ln = Eu, Gd, Tb, Dy) with beta-diketonate ligands was continued. The photophysical and photochemical properties of the new materials were studied at FCT/UNL.

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## Glass Science with Applications in Art Studies

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In 2010, A. Pires de Matos continued as coordinator of the Research Unit “VICARTE-Glass and Ceramics for the Arts”. Work was carried out by members of ITN and FCT/UNL mainly in the development of new materials for artistic applications.

Gold ruby glass doped with lanthanide oxides obtained by gamma irradiation: To sodalime silicate glasses containing different concentrations of gold, cerium, europium and samarium oxides were added. The samples were irradiated with gamma rays in order to obtain nanoparticles of gold. The influence of the lanthanide oxides in the colour striking was studied. The effect of the investigated lanthanide oxides on the reduction of the gold ions to metal was interpreted considering pertinent redox equilibria and the Ellingham diagrams for the lanthanide oxides.

Synthesis of copper ruby glass using gamma radiation: To a batch of raw materials used to prepare soda lime silicate glass, cuprous oxide was added. After irradiation with gamma rays and thermal treatment at about 600ºC a red colour was obtained which was due to nanoparticles of copper. When cupric oxide was used no reduction was observed.

VICARTE

Following the objectives of the project “Glass in Art: Light and Colour” (POCI/EAT/60496/2004), thin-layer deposition on glass was made using the spray-pyrolysis technique. The first experiments with copper acetate in methanol and water gave origin to a thin layer deposition of copper oxide which after heating at about 600ºC gave origin to nanoparticles of copper.

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[1] IOC Group/UCQR-ITN & VICARTE, FCT-UNL. [2] VICARTE, FCT-UNL. [3] REQUIMTE, FCT/UNL. [4] RTPP Group/UFA-ITN.