

Inorganic and Organometallic Chemistry

Noémia Marques and Joaquim Marçalo

The activities of the Group comprise the synthesis, characterisation and chemical reactivity studies of inorganic, organometallic and intermetallic compounds of actinides and lanthanides with the aim of understanding the influence of the electronic structure and the size of these elements in the chemical properties of their compounds. Chemical reactivity is assessed by stoichiometric reactions and by homogeneous and heterogeneous catalytic studies, which are also carried out in an effort to find new applications for lanthanide and actinide compounds. Gas-phase ion chemistry studies with the same elements and studies of the energetics of their compounds, using advanced mass spectrometric and calorimetric techniques, are also undertaken with the same objective.

Relevant facilities maintained by the Group are a laboratory for handling macroscopic quantities of the more radioactive actinides, a laboratory for catalytic studies, prepared for work with CO, a laboratory for calorimetric studies and thermal analysis, and two select mass spectrometers, a Fourier transform ion cyclotron resonance (FTICR) instrument, equipped with electron ionisation (EI) and laser desorption/ionisation (LDI) sources and a quadrupole ion trap (QIT) instrument, equipped with electrospray ionisation (ESI) and atmospheric pressure chemical ionisation (APCI) sources. The QIT mass spectrometer was acquired with the support of the "National Program for Scientific Hardware Renewal" of FCT and is part of the National Mass Spectrometry Network.

FTICR/MS studies were pursued and the first gas-phase synthesis and characterization of mono and polymetallic uranium oxide anions was achieved via LDI of ammonium uranate. The structures of these new uranates were probed by collision induced dissociation (CID) experiments and by reactivity studies with methanol. QIT/MS studies using ESI were initiated and several ionic species generated from thorium, uranyl and lanthanide nitrates in water/methanol solutions were characterized in the gas-phase by CID and condensation reactions with the solvent molecules.

A collaboration study with FCUL and ITQB, using the FTICR/MS facility, doubtless concluded that non protic ionic liquids in the gas-phase behave as neutral ion pairs in opposition to the behaviour of protic ionic liquids. This fact supports the possibility to fractionally distil ionic liquids and will lead to new studies on alkali-metal ionic liquids that reveal a completely unexpected behaviour in a new project supported by FCT.

Studies on the reactivity of yttrium, samarium and uranium complexes with the mono-functionalized tacn ligand [O(3,5-tBu₂Ph)}-tacn(¹Pr₂)] continued. Alkyl and silyl derivatives of yttrium complexes supported by the bis(phenolate)diamine ligand (^tBu₂O₂NN'([Me₂N(CH₂)₂N{CH₂-(2-OC₆H₂-Bu¹₂-3,5)₂}]]) showed to be very active catalysts for the polymerization of ε-caprolactone. Multicoordinate ligands for actinide/lanthanide separations were explored and were the subject of a MSc thesis presented at IST in October 2007.

Pursuing previous work, studies of CO₂ as C1 feedstock were performed, namely through the selective oxidation of methane (OCM reaction) on UFe₂, UFe₂Sn and UFe₅Zn₇.

The collaboration with the Radiation Technologies: Processes and Products Group (Physics Sector) in the study of the gamma radiation effect on several waste water sources was pursued. The collaboration with OMNIDEA, Lda., a start-up company dedicated to R&D of aerospace technology and energy systems continued and a ITN-OMNIDEA cooperation protocol was established.

Joint projects with the Research Unit "Glass and Ceramic for the Arts" (a collaboration between ITN, FBAUL and FCT/UNL) on new lanthanide based fluorescent glasses, on ruby glass and on provenance studies of Portuguese glasses continued.

An important part of the activity of the Group is the training of young research students. Some of the group members are involved in undergraduate and post-graduate university courses. The work is financially supported by FCT, via research projects and PhD and Post-doc grants.

Research Team

Researchers

N. MARQUES, Princ., Group Leader (Jan.-Oct.)
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Gas-Phase Ion Chemistry of Actinides and Lanthanides

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Objectives

The gas-phase chemistry of atomic and molecular actinide and lanthanide ions is studied in order to obtain mechanistic, kinetic and thermodynamic information that can be correlated with the electronic structures of the ions and compared with data from condensed phases. The experimental work is based on the use of advanced mass-spectrometry techniques, namely, Laser Desorption/Ionization Fourier Transform Ion Cyclotron Resonance MS (LDI-FTICR/MS) and Electrospray Ionization Quadrupole Ion Trap MS (ESI-QIT/MS). For the actinides, the specific aims are to produce novel species with new ligations and properties, to probe the participation of the 5f electrons in chemical bonding in the first half of the series, and to estimate thermodynamic data for species that may be of interest for condensed-phase processes. Parallel theoretical studies of selected actinide molecular ions are also carried out via collaborations to substantiate the interpretation of the experimental observations.



FTICR mass spectrometer

Results

The FTICR/MS studies of the chemistry and thermochemistry of atomic and molecular actinide ions done in recent years in our laboratory were summarized [1]. A highlight of the work, the first combined experimental and theoretical demonstration of the active role of 5f electrons in organoactinide chemistry, was described in detail [2].

On the experimental side, FTICR/MS studies were pursued and the first gas-phase synthesis and characterization of mono and polymetallic uranium oxide anions was achieved via LDI of ammonium uranate, $(\text{NH}_4)_2\text{U}_2\text{O}_7$ [3]. The new species, which can also be considered members of the uranate family, had the general formulas $\text{U}_x\text{O}_{3x}^-$, where $x = 1-6$, $\text{U}_x\text{O}_{3x+1}^-$, where $x = 1$, and $\text{U}_x\text{O}_{3x-1}^-$, where $x = 3-8$. The structures of these new uranates were probed by collision induced dissociation experiments and by reactivity studies with methanol. The mechanisms of the sequential reactions with methanol were studied in detail using $\text{C}^2\text{H}_3\text{OH}$ and $\text{CH}_3^{18}\text{OH}$. Most notably, in the case of UO_3^- , formation of an elusive hydride species with formula $\text{UO}_2(\text{OH})\text{H}^-$ was observed;

theoretical studies performed by M. D. C. Michellini and N. Russo at the University of Calabria confirmed the hydride structure. In the reactions of the anionic clusters, addition of up to three methoxide ligands per U atom was observed; this gas-phase reactivity of polymetallic uranates mimics the condensation of methanol on uranium oxide surfaces (J. A. Lloyd, W. L. Manner, M. T. Paffett, *Surf. Sci.* 423 (1999) 265-275).



QIT mass spectrometer

A new QIT mass spectrometer was installed in the Actinide Chemistry laboratory. It was acquired with the support of the “National Program for Scientific Hardware Renewal” of FCT and is part of the National Mass Spectrometry Network. This instrument is equipped with atmospheric pressure ion sources, ESI and APCI, which allow the study of ions in solution. Several experiments with thorium, uranyl and lanthanide nitrates in water/methanol solutions were performed, which included the gas-phase characterization of several ionic species by collision induced dissociation experiments and condensation reactions with the solvent molecules.

Published work

J. K. Gibson, R. G. Haire, J. Marçalo, M. Santos, J. P. Leal, A. Pires de Matos, R. Tyagi, M. K. Mrozik, R. M. Pitzer, B. E. Bursten, FTICR/MS studies of gas-phase actinide ion reactions: fundamental chemical and physical properties of atomic and molecular actinide ions and neutrals, *Eur. Phys. J. D* 45 (2007) 133-138.

J. K. Gibson, R. G. Haire, J. Marçalo, M. Santos, A. Pires de Matos, M. K. Mrozik, R. M. Pitzer, B. E. Bursten, Gas-phase reactions of hydrocarbons with An^+ and AnO^+ ($\text{An} = \text{Th}, \text{Pa}, \text{U}, \text{Np}, \text{Pu}, \text{Am}, \text{Cm}$): the active role of 5f electrons in organoprotactinium chemistry, *Organometallics* 26 (2007) 3947-3956.

J. K. Gibson, Fundamental aspects of 5f-element chemistry revealed by gas-phase reactions of actinide ions, *Winter School in Theoretical Chemistry 2007 - Actinide Chemistry*, University of Helsinki, Dec. 2007 (http://www.chem.helsinki.fi/~sundholm/winterschool/lecture_notes_2007/Gibson_Helsinki_Dec.2007.ppt).

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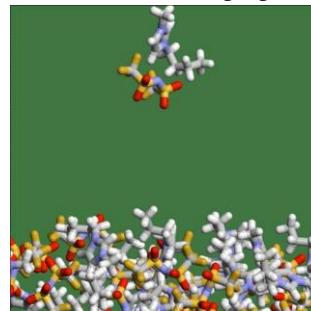
Molecular Energetics of Organic, Inorganic and Organometallic Compounds

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The main objective of this research line is to collect data and rationalize it in a systematic way that enables a deeper knowledge of the energetics of molecules (both inorganic and organic compounds). Special importance is 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 and hydrocarbons were studied.

During 2007, all enthalpies of formation published for CH and CHO compounds were critically revised and used to improve an extended Laidler method of additive contributions. An *on-line* database with all these values is in progress. New routes for fluoroapatite synthesis were explored and their thermal and structural properties studied. The determination of the enthalpies of formation of several polyalkoxides, $M_x[O(CH_2)_nO]_y$ ($n=2-8$, $x=1$, $y=1$ or $x=2$, $y=3$) with alkaline-earth and lanthanides began, being one of the calcium compound already synthesized. Also, new studies on the gas-phase acidity of substituted phenols were undertaken using FTICR/MS.

A collaboration study with FCUL and ITQB, using the FTICR/MS facility, doubtless concluded that non protic ionic liquids in the gas-phase behave as neutral ion pairs in opposition to the behaviour of protic ionic liquids. This fact supports the possibility to fractionally distil ionic liquids and will lead to new studies on alkali-metal ionic liquids that reveal a completely unexpected behaviour in a new project supported by FCT.



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f-Element Chemistry with Multidentate Nitrogen and Oxygen Donor Ligands

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The search for renewable, biodegradable polymers has increased in recent years. In this context, we have been investigating the catalytic activity of lanthanide complexes supported by the bis(phenolate)diamine ligand ($^{tBu_2}O_2NN'$ ($[Me_2N(CH_2)_2N\{CH_2-(2-OC_6H_2-Bu^1-3,5)_2\}]$)) in the polymerization of cyclic esters. The complex $[YCl(O_2^{tBu_2}NN')(DME)]$, and the silyl $[Y(^{tBu_2}O_2NN')(N(SiMe_3)_2)]$ and alkyl $[Y(^{tBu_2}O_2NN')(C_6H_4CH_2NMe_2)]$ derivatives have been synthesized. Both derivatives showed to be active catalysts for the polymerization of ϵ -caprolactone giving 100% conversion. In contrast the samarium analogues were not active. This result was understandable when we found that the attempted preparation of the corresponding silyl and alkyl derivatives of $[Sm(^{tBu_2}O_2NN')Cl]_x$ resulted in formation of the bimetallic compounds $[Sm(^{tBu_2}O_2NN')_2]M$ ($M = Li, K$), that are completely inactive in the polymerization of ϵ -caprolactone.

Studies on oxidative chemistry of the f-elements with nitrogen donor ligands continued. (A. Domingos, I. Lopes, J. C. Waerenborgh, N. Marques, G. Y. Lin, X. W. Zhang, J. Takats, R. McDonald, A.C. Hillier, A. Sella, M.R.J. Elsegood, V.W. Day, *Inorg. Chem.* **2007**, *46*, 9415-9424; M. A. Antunes, PhD thesis, FCUL, Feb. 2007). Multicoordinate ligands for actinide/lanthanide separations were explored (B. J. C. Vieira, MSc thesis, IST, Oct. 2007).

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f-Block Element Intermetallic Compounds as Catalysts

J. Branco, A. P. Gonçalves¹

Intermetallic compounds of lanthanide or actinide metals combined with d metals have been found to be active in a variety of reactions. The main objective of this project is (i) to make a systematic study of the f block elements behavior as catalysts or catalytic precursors and (ii) to develop new methods for the preparation of 4f and 5f nanostructured materials for catalytic purposes.

Pursuing previous work, we have studied the oxidative coupling of methane (OCM reaction) on UFe_2 , UFe_2Sn and UFe_5Zn_7 using CO_2 and CH_4 as C1 feedstocks. Preliminary results at 850 °C indicate that, at isoactivity, the selectivity to C2 ($C_2H_4+C_2H_6$) and the selectivity to C_2H_4 is higher on the ternary compounds, e.g. selectivity C2 / C_2H_4 , 36 / 33 % on UFe_2 and C2 / C_2H_4 , 58 / 58 % on UFe_5Zn_7 .

¹ Solid State Group, Chemistry Sector., ITN.

Glass Science with Applications in Radioactive Waste Vitrification, Archaeometry and Art Studies

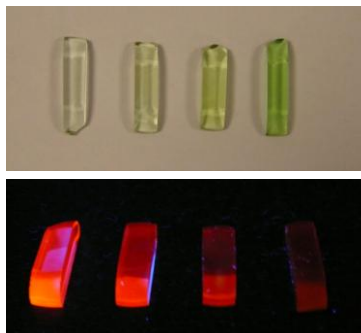
A. Pires de Matos, J. Marçalo, F. Lopes, A. Ruivo¹, V. S. Muralha¹

A. Pires de Matos is coordinating the research unit VICARTE - “Glass and Ceramics for the Arts”, supported by FCT, with participants from ITN, FBAUL and FCT/UNL. Expertise on glass science is being developed, particularly in the synthesis of glasses with new properties and in chemical characterisation of glasses for provenance studies.

In 2007 the archaeometric studies of portuguese glasses using several techniques continued. The study of Coia glasses and the comparison with glasses from Marinha Grande was the main objective; XRF, atomic absorption spectrometry and ICP/MS (collaboration with IPIMAR) were used for their characterization. A micro-destructive method was also developed, sampling minute amounts of glass and analysing their composition by neutron activation analysis. The first experiments dealt with the determination of sodium (collaboration with the Nuclear Reactor Department, ITN).

Within the project “Provenance Studies of Portuguese Glasses”, uranium glass objects were characterized by XRF. Dose rates were measured in contact and at several distances in a set of 20th century glass objects containing uranium (collaboration with the DPSRN, ITN).

Another research area is related with the development of glasses for artistic applications. Studies on luminescent glasses with rare earths have continued, as well as the quenching of luminescence by d-transition elements. Gold ruby glass was synthesized using gamma radiation for reduction of gold ions and to improve nucleation of the gold nano-particles (collaboration with the Department of Physics, ITN).



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Gamma Irradiated Chitosan/pHEMA Membranes for Drug Release Systems

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To obtain biocompatible and sterilized matrices for controlled drug release to be used in direct contact with skin, membranes with different contents in chitosan and hydroxyethyl methacrylate (HEMA) have been prepared by γ irradiation from a ⁶⁰Co source. Those membranes naturally exhibit antimicrobial properties with good mechanical behavior. The loading with amoxicillin led to active membranes that show an insignificant level of hemolysis and present a fast rate of amoxicillin release. Studies on the influence of membrane thickness show that an optimal thickness for each membrane composition can be obtained. At these conditions a maximum loading and release of amoxicillin was achieved.



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