

# Inorganic and Organometallic Chemistry

*António Pires de Matos*

The activities of the group comprise the synthesis, characterization and chemical reactivity studies of inorganic, organometallic and intermetallic compounds of **actinides** and **lanthanides** in order to understand the influence of the electronic configuration and of the size of these elements in the chemical behaviour of their compounds. Chemical reactivity is assessed by stoichiometric reactions and by homogeneous and heterogeneous catalytic studies. Gas phase ion chemistry studies with the same elements and the study of the energetics of f-element compounds are also made with the same objective.

Although the dominant research activity of the group has a fundamental nature, the type of chemistry we are dealing with allowed us to envisage applications either in nuclear sciences or in catalysis, materials science and environment. Whereas, within the actinides, our studies have been centred on uranium and thorium, we intend to extend the gas phase chemistry to the more toxic actinides. At the same time we are trying to explore the very interesting catalytic properties of some uranium, thorium and lanthanide compounds.

The work made during 2000 can be summarized as follows:

Studies on the reactivity of hydrotris(pyrazol-1-yl)borate anchored lanthanide (II) compounds have been pursued. We were successful in preparing new  $\text{Sm}(\text{Tp}^{\text{Me}2})_2\text{X}$  compounds by one-electron-transfer reactions of  $\text{Sm}(\text{Tp}^{\text{Me}2})_2$  with reducible organic substrates and in accessing to a new class of mixed-ligand Ln(II) derivatives by application of the sterically demanding  $\text{Tp}^{\text{Ms}}$  and  $\text{Tp}^{\text{Ms,Me}}$  ligands. These studies have been the subject of a PhD thesis to be presented at the beginning of 2001.

The synthesis and characterization of polynuclear lanthanide alkoxides and aryloxides using the metal vapour synthesis technique and reactions of the metals in liquid ammonia were continued. The liquid ammonia process seems to be a convenient route to lanthanide aryloxide complexes. The polymetallic lanthanide compounds  $[\text{Eu}_4(\mu\text{-OC}_{10}\text{H}_7)_6(\text{OC}_{10}\text{H}_7)_2(\text{C}_4\text{H}_8\text{O})_{10}].2(\text{C}_4\text{H}_8\text{O})$  and  $[\text{Yb}_2(\mu\text{-OC}_{10}\text{H}_7)_2(\text{OC}_{10}\text{H}_7)_4(\text{C}_4\text{H}_8\text{O})_2(\text{CH}_3\text{CN})_2]$  were synthesized and characterized by X-ray diffraction studies. These studies have been the subject of a PhD thesis to be presented at the beginning of 2001.

There is a relevant amount of thermochemical data for alkoxides, but almost no data for thiolates. During 2000 measurements on alkaline metal thiolates were made that can be used as models to estimate enthalpies of formation of lanthanide thiolates. Also, the conception and design of a solid thermal bath conduction calorimeter was undertaken, and a prototype started to be constructed. This apparatus will allow to measure the energetics of catalytic reactions over the same samples that are being studied for chemical reactivity.

During this year the catalytic work has been centred in the study of binary intermetallic compounds of actinides ( $\text{ThNi}_2$ ,  $\text{UNi}_2$ ) and lanthanides ( $\text{LnNi}$ ,  $\text{Ln}=\text{Pr}$ ,  $\text{Gd}$ ,  $\text{Tm}$ ) using the selective isoprene hydrogenation as model reaction. The results obtained clearly show that the lanthanide presence in the intermetallic enhances the reaction rate, with a promoting effect on the nickel activity that decreases going from Pr to Tm. The activity is highest on the actinide intermetallic compounds being  $\text{ThNi}_2$  more active than the analogous uranium compound. This is the first time that such results are reported for 5f block elements.

Gas-phase ion chemistry studies with lanthanide and actinide species, using the FT-ICR/MS technique, were pursued and included ligand exchange experiments involving pentamethylcyclopentadiene, indene and cyclooctatetraene and selected lanthanide cations, reactivity studies of thorium and uranium cations with isopropanol, synthesis of mixed iron-lanthanide or actinide bimetallic oxide cations by laser desorption/ionisation, and uranium speciation studies in aqueous solutions using electrospray and laser ionisations.

Seven projects were submitted to external funding agencies (FCT and SPV). Five projects were approved and one is still waiting for evaluation. Four projects are coordinated by our Group; one is in collaboration with the industry. As a consequence 5 new research students will be admitted in January 2001. A post-doctoral position for 2001 was also funded by NATO.

## Research Team

### Researchers

- António Pires de Matos (Coordinator Researcher) (**Group Leader**) - synthesis, reactivity and FTICR/MS studies of An and Ln compounds
- Ângela Domingos (Principal Researcher) - X-ray crystallography
- Noémia Marques (Principal Researcher) - synthesis and reactivity of actinide and lanthanide compounds.
- Joaquim Branco (Aux. Researcher) - synthesis, reactivity and catalytic studies with actinide and lanthanide compounds.
- Joaquim Marçalo (Aux. Researcher) - FTICR/MS, gas phase ion chemistry.
- João Paulo Leal (Aux. Researcher) - thermochemistry and FTICR/MS.
- Teresa Almeida Gasche (Aux. Researcher) - characterization of actinide and lanthanide catalysts.
- José Manuel Carretas (Research Assistant)<sup>1</sup> - synthesis of lanthanide alkoxides and aryloxides.

<sup>1</sup> Doing PhD.

### Students

- Irene Lopes (PRAXIS PhD Research Student)

### Technical Personnel

- Adelaide Carvalho
- António Soares

### Publications

Journals:	6	and 5 in press
Other publications:	1	
Communications:	11	
Theses:	1	

### Funding

	<b>×10<sup>3</sup> PTE</b>
<b>Research Projects<sup>(a)</sup>:</b>	3015
<b>Services:</b>	125
<b>TOTAL:</b>	<b>3140</b>

(a)

	<b>×10<sup>3</sup> PTE</b>
- Chemical Behaviour in the Heterogeneous Phase of Compounds of the f Elements (PRAXIS XXI 2/2.1/QUI/386/94) - (1997-2000) (27 000 × 10 <sup>3</sup> PTE → ITN/15 680 × 10 <sup>3</sup> ) ITN/Co-ordinator: <b>A. Pires de Matos</b> , Partners: UNL, IST, ISEL.....	1015
- Structure and Reactivity of Glycosidic Derivatives of Flavonoids and Their Synthetic Analogues: A Fundamental Investigation by MS Techniques (PRAXIS XXI 2/2.1/QUI/119/94) (1998-2001) (18 479 × 10 <sup>3</sup> → ITN/2000 × 10 <sup>3</sup> ) Project Co-ordinator: FCUL (M.A. Almoester Ferreira), Partner: ITN ( <b>A. Pires de Matos, J. Marçalo</b> ): .....	2000

## Synthesis and Characterization of Polynuclear Lanthanide Alkoxides and Aryloxides

José Carretas, Joaquim Branco, João Paulo Leal, Joaquim Marçalo,  
 Ângela Domingos, António Pires de Matos

### Objectives

There is a growing interest toward the search for alternative ligands, in particular alkoxides and aryloxides, to cyclopentadienyl ligands in organolanthanide chemistry. The applications of lanthanide alkoxides and aryloxides are diverse, ranging from catalysis of organic reactions to synthesis of high purity oxide materials. In this work, we are studying the reactivity of lanthanide metals toward several alcohols and phenols.

### Results

The reactions of europium and ytterbium in liquid ammonia with a solution of 1-naphthol in thf provide a convenient route to lanthanide aryloxide complexes. The polymetallic lanthanide compounds **1**  $[\text{Eu}_4(\mu\text{-OC}_{10}\text{H}_7)_6(\text{OC}_{10}\text{H}_7)_2(\text{C}_4\text{H}_8\text{O})_{10}]\cdot 2(\text{C}_4\text{H}_8\text{O})$  (Figure 1) and **2**  $[\text{Yb}_2(\mu\text{-OC}_{10}\text{H}_7)_2(\text{OC}_{10}\text{H}_7)_4(\text{C}_4\text{H}_8\text{O})_2(\text{CH}_3\text{CN})_2]$  (Figure 2) were synthesized and characterized by X-ray diffraction studies. X-ray quality crystals were grown respectively, from a solution of **1** in thf at room

temperature and from a solution of **2** in  $\text{CH}_3\text{CN}$  at  $-20^\circ\text{C}$ . In the dimeric and the tetrameric structures all the metallic centers are hexacoordinated. The oxidation states of the divalent europium and the trivalent ytterbium are in agreement with their different reduction potentials. [1]

### Published (or in press) work

[1] Carretas, J. M., Branco, J., Marçalo, J., Isolani, P. C., Domingos, A., Pires de Matos, A., Synthesis and Characterization of Polynuclear Lanthanide Aryloxides, *J. Alloys and Compounds*, in press.

### Further Work

We intend to complete the EXAFS studies of the compounds where no single crystals can be obtained. The synthesis and characterization of bimetallic f block element aryloxides and alkoxides will be undertaken.

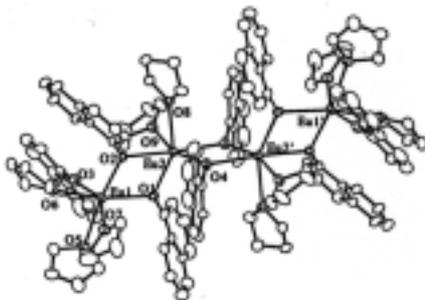


Figure 1. ORTEP diagram of  $[\text{Eu}_4(\mu\text{-OC}_{10}\text{H}_7)_6(\text{OC}_{10}\text{H}_7)_2(\text{THF})_{10}]\cdot 2\text{THF}$ .

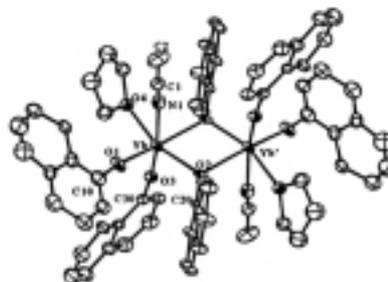


Figure 2. ORTEP diagram of  $[\text{Yb}_2(\mu\text{-OC}_{10}\text{H}_7)_2(\text{OC}_{10}\text{H}_7)_4(\text{THF})(\text{NCMe})_2]\cdot 2\text{NCMe}$ .

## Chemical Behaviour of *f*-Block Element Intermetallic Compounds

Joaquim Branco, Teresa Almeida Gasche, António Pires de Matos

### Objectives

Binary intermetallic compounds of lanthanides or actinides and d transition metals (usually Ni, Cu, Co, Zn) have been found to be catalytic active in a range of reactions. The main goal of this project is to study different AB and AB<sub>2</sub> intermetallic compounds, containing lanthanides and actinides, in order to understand the influence of the f block element (electronic configuration and variation in size) in the chemical behaviour of those compounds. We report the first results on the selective isoprene hydrogenation over LnNi (Ln=Pr, Gd, Tm), ThNi<sub>2</sub> and UNi<sub>2</sub>.

### Results

The lanthanide and actinide intermetallic compounds are more active than pure nickel. The lanthanide intermetallic compounds are 3 to 20 times more active than Ni. The activity and selectivity (at isoprene isoconversion) to isopentenes decreases going from Pr to Tm. The f block element clearly enhances isoprene hydrogenation, with a promoting effect on pure nickel activity and modification of product distribution. The selectivity to 2-methyl-2-butene and 2-methyl-1-butene, important products for the TAME process, is always greater than 90% [1].

The highest activity is observed over the actinide intermetallic compounds. Isoprene is hydrogenated more quickly over the thorium catalysts than on the uranium catalyst. ThNi<sub>2</sub> is particularly active for isoprene hydrogenation. On the actinide intermetallic compounds the selectivity is very different. The main reaction products are 2-methyl-2-butene and isopentane. The selectivity to isopentenes is unfavourable and decreases over these compounds: Ni (100%), UNi<sub>2</sub> (68%), and ThNi<sub>2</sub> (38%). This is the first time that such results are reported for intermetallic compounds with f elements [2].

### Published (or in press) work

- [1] Branco, J. B., Almeida Gasche, T., Gonçalves, A. P., T., Pires de Matos, A., Selective Isoprene Hydrogenation over LnNi (Ln=Pr, Gd, Tm) Intermetallic Compounds, *J. Alloys and Compounds*, in press.
- [2] Almeida Gasche, T., Branco, J. B., Gonçalves, A. P., T., Pires de Matos, A., Selective Isoprene Hydrogenation over AnNi<sub>2</sub> (An=Th, U) Intermetallic Compounds, *4<sup>th</sup> International Conference on f-Elements - ICFE'4*, Madrid, Spain, September 2000 (Poster).

### Further Work

Work is in progress to understand the reaction mechanisms that are responsible for these observations.

The study of "Oxidative Coupling of Methane using f Block Element Intermetallic Compounds as Catalytic Precursors" will be undertaken (PCTI/QUI/35394/99).

## Energetics of f-Element Compounds

J. P. Leal, H. Raminhos<sup>a</sup>

### Objectives

The main objective of the project is to foster the knowledge of energetics on f-element compounds (both on solid state and in solution). To achieve this goal both lanthanide and actinide organometallic and intermetallic compounds were studied. Also alkaline and alkaline-earth compounds (alkoxides, phenoxides, thiolates and cyclopentadienyls) will be addressed in order to provide adequate models that allow a deeper understanding and improve our capability of prediction of properties.

### Results

During 2000 the work followed different paths to achieve the stated objectives. Following the determination of bond enthalpies in uranium organometallic compounds  $[U_2X\{HB(Me_2-pz)_3\}_2]$ , X = OR, I and Cl] by reaction-solution calorimetry efforts were made to clarify the final state of some of the studied reactions. To develop a large enough database of alkaline and alkaline-earth metal compounds that permit to predict, with a high precision, enthalpies of formation for new lanthanide alkoxides, some additional enthalpies of formation of lithium, sodium, potassium, rubidium and caesium alkoxides, phenoxides, thiolates and substituted cyclopentadienyls were studied. These values will continue to be used to check a previously developed model (J.P. Leal, J.A. Martinho Simões, *J. Organomet. Chem.* **460** (1993) 131) to estimate the enthalpies of formation of organometallic species [1,2].

Some development of equipment was made (conception and design of a solid state thermal bath conduction calorimeter) that will allow to make thermal analysis and gas chromatography over the same sample.

Together with other researchers of ITN and several university partners from half a dozen different universities a project for an accredited thermal measurements laboratory at ITN was prepared. With this project we intend to foster the interdisciplinary contribution of different expertise existing at ITN and confirm a strong investment on quality. This project is under evaluation.

### Published (or in press) work

- [1] Barreira, T., Leal, J.P., Standard molar enthalpies of formation of Mg and Ca alkoxides, *Eur. J. Inorg. Chem.* (2000) 987.
- [2] Carvalho, A., Cachata, V., Leal, J.P., Standard molar enthalpies of formation of Li, Na, K and Tl cyclopentadienyls, *Eur. J. Inorg. Chem.*, in press.

### Further work

In the future we intend to continue our studies on lanthanide and actinide compounds (both organometallics and intermetallics). The metal alkoxide work will be expanded to lanthanide metals. We will keep also a renewed interest on alkaline and alkaline-earth compounds because they proved to be very good models to understand f-element compounds.



Reaction-solution calorimeter cell

\* Graduate student, Faculdade de Ciências da Universidade de Lisboa.

## Reactivity of Lanthanide Compounds

Irene Lopes, Ângela Domingos, Noémia Marques

### Objectives

The aim of this project is to study the reactivity of lanthanide compounds stabilized by hydrotris(pyrazolyl)borate ligands. Previous results obtained in this laboratory on the reactivity of  $\text{Sm}(\text{Tp}^{\text{Me}_2})_2$  (**1**) ( $\text{Tp}^{\text{Me}_2} = \text{HB}(3,5\text{-Me}_2\text{pz})_3$ ) toward unsaturated organic substrates led to the synthesis and characterization of a series of  $\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{X})$  compounds in which X is the radical form of the ligand X ( $\text{X} = \text{OCPh}_2$ ,  $\text{OC}_{13}\text{H}_8$ ,  $p\text{-OC}_6\text{H}_4\text{O}$ ). It was also shown that **1** leads to reductive cleavage of  $\text{E}_2\text{R}_2$  reagents affording chalcogenolate derivatives[1]. It was found that **1** reacts with  $\text{TiCp}$  to yield the first mixed Tp/Cp compound,  $\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{Cp})$ . The thermolysis of this compound in the solid led to formation of  $\text{Sm}(\text{Tp}^{\text{Me}_2})[\text{HB}(3\text{-}5\text{Me}_2\text{pz})_2(\text{C}_5\text{H}_4)]$ , a compound in which the Sm is coordinated to a Tp ligand and to a novel, dianionic ligand,  $\text{HB}(3\text{-}5\text{Me}_2\text{pz})_2(\text{C}_5\text{H}_4)$ , due to C-H activation mediated by the metal centre[2].

Another goal of this project was to synthesize mono-ligated Yb(II) compounds. This goal was achieved by reacting ytterbium diiodide with the ligands  $[\text{HB}[(3\text{-Mspz})_3] (\text{Tp}^{\text{Ms}})]$  and  $[\text{HB}[(3\text{-Mspz})_2(5\text{-Mspz})] (\text{Tp}^{\text{Ms}^*})]$ . The compounds  $\text{YbI}(\text{Tp}^{\text{Ms}})(\text{THF})_2$  and  $\text{YbI}(\text{Tp}^{\text{Ms}^*})(\text{THF})_2$  were synthesized, but  $\text{YbI}(\text{Tp}^{\text{Ms}})(\text{THF})_2$  is unstable in THF solution leading to  $\text{YbI}(\text{Tp}^{\text{Ms}^*})(\text{THF})_2$  due to isomerization of the ligand. To hinder the isomerization reaction the new ligands  $[\text{HB}[(3\text{-Ms},5\text{-Mepz})_3] (\text{Tp}^{\text{Ms},\text{Me}})]$  and  $[\text{HB}[(3\text{-Ms},5\text{-Mepz})_2(3\text{-Me},5\text{-Mspz})] (\text{Tp}^{\text{Ms},\text{Me}^*})]$  were prepared. In this case, due to the additional inductive effect of the methyl substituents, the isomerization reaction was not observed and the two compounds ( $\text{YbTp}^{\text{Ms},\text{Me}})(\text{THF})_2$  and  $\text{YbI}(\text{Tp}^{\text{Ms},\text{Me}^*})(\text{THF})_2$  were isolated[3].

### Results

The above studies with **1** were extended to other substrates. **1** undergoes readily one-electron transfer reactions with benzaldehyde azine, pyridazine ( $\text{N}_2\text{C}_4\text{H}_4$ ), isothiocyanate and 2-2'-bipyridine. Different reactivity patterns were found: stabilization of a radical species with benzaldehyde azine, ( $\text{Sm}(\text{Tp}^{\text{Me}_2})_2[\text{PhC}(\text{H})=\text{N}-\text{N}=\text{C}(\text{H})\text{Ph}]$ ) (**2**), coupling reactions between two radical anions which bridges two samarium centres in the reactions of  $\text{Sm}(\text{Tp}^{\text{Me}_2})_2$  with pyrazine and isothiocyanate,  $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]_2[\mu,\eta^2\text{-N}_2\text{C}_4\text{H}_4\text{-}_2]$  (**3**) and  $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]_2[\mu,\eta^2\text{-N}(\text{Ph})\text{CS-}_2]$  (**4**) or ionic species of the type  $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]^+[(\text{bipy})_3]^-$

(**5**).  $\text{Sm}(\text{Tp}^{\text{Me}_2})_2$  does not react with protic substrates, but we have found that  $\text{Sm}(\text{Tp}^{\text{Me}_2})_2\text{Cl}$  reacts with potassium alkyls to give  $\text{Sm}(\text{Tp}^{\text{Me}_2})_2\text{R}$  which are unstable due to reductive cleavage of the Sm-C bond. In spite of its instability these species have a life time long enough to be used as intermediates for reactions with protic substrates, such as alcohols, amines and alkynes. By this way we have synthesized the following compounds:  $\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{OC}_6\text{H}_2\text{-}2,4,6\text{Me}_3)$  (**6**),  $\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{NPh}_2)$  (**7**), and  $\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{CCPh})$  (**8**).

Reactivity studies of the previously reported  $\text{YbI}(\text{Tp}^{\text{Ms}^*})(\text{THF})_2$  and  $\text{YbI}(\text{Tp}^{\text{Ms},\text{Me}})(\text{THF})_2$  have been pursued. The derivative  $\text{Yb}[\text{N}(\text{SiMe}_3)_2](\text{Tp}^{\text{Ms}^*})$  (**9**) has been synthesized. **9** reacts with CpH, indene and HCl to yield  $\text{Yb}(\text{Cp})(\text{Tp}^{\text{Ms}^*})$  (**10**),  $\text{Yb}(\text{C}_9\text{H}_7)(\text{Tp}^{\text{Ms}^*})$  (**11**) and  $[\text{Yb}(\text{Tp}^{\text{Ms}^*})(\mu\text{-Cl})_2]$  (**12**), respectively. **12** has an unusual molecular structure, the steric and electronic unsaturation of the ytterbium centre being compensated by additional interactions of the metallic centres with a carbon atom of one mesityl group.

### Published (or in press) work

- [1] Lopes, I., Hillier, A.C., Liu, S.Y., Domingos, A., Ascenso, J., Galvão, A., Sella, A., Marques, N., Solid State Structure and Solution Behaviour of Eight-Coordinate Sm(III) Poly(pyrazolyl)borate Compounds, *Inorg. Chem.*, in press.
- [2] Lopes, I., Lin, G. Y., Domingos, A., Marques, N., Takats, J., Unprecedented Transformation of a Hydrotris(pyrazolyl)borate Ligand at a Metal Center: Synthesis and Rearrangement of the First Mixed Tp / Cp Lanthanide Complex,  $\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{Cp})$ , *J. Am. Chem. Soc.* **121** (1999) 8110-8111. This finding led to the submission of a project to FCT which has been funded (2001-2003).
- [3] Lopes, I., Domingos, A., Marques, N., Hydrotris(3-Mesitylpyrazolyl)borate Ytterbium (II) Derivatives, *4<sup>th</sup> International Conference on f-elements*, Madrid, Sep.2000.

### Further work

Synthesis of mixed pyrazolylborate/cyclopentadienyl dianionic ligands. Use of the ligands as a cyclopentadienyl replacement species in lanthanide chemistry.

## Gas Phase Ion Chemistry of Lanthanides and Actinides

Joaquim Marçalo, António Pires de Matos, José Manuel Carretas,

### Objectives

As a contribution to a better knowledge of the chemistry of the lanthanide (Ln) and actinide (An) series elements, we have been studying the gas phase reactivity with organic molecules of ions of metals, metal oxides, metal oxide clusters, intermetallic and organometallic compounds of these elements. Special attention has been given to the kinetics, mechanisms and energetics of the reactions, that we have tried to correlate with the electronic structure of the ions and to compare with analogous processes occurring in condensed phases. The experimental work has been based on the use of Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR/MS), a technique that is specially suited for the study of the chemistry of ion-molecule systems in the gas phase. We have also been exploring, through international collaborations, the use of electrospray ionisation (ESI) coupled to FT-ICR/MS to study different aspects of the gas phase chemistry of Ln and An compounds, taking advantage of the ability of ESI to transfer solution species to the gas phase.

### Results

Gas-phase ligand exchange experiments involving pentamethylcyclopentadiene, indene and cyclooctatetraene and selected lanthanide cations ( $\text{Pr}^+$ ,  $\text{Sm}^+$ ,  $\text{Tb}^+$ ,  $\text{Ho}^+$ ,  $\text{Yb}^+$ ,  $\text{Lu}^+$ ) were performed to extend previous studies in gas-phase chemistry of lanthanide metallocenes.<sup>1</sup>

Gas-phase reactivity studies of  $\text{Th}^+$  and  $\text{U}^+$  cations with isopropanol, including kinetic and mechanistic experiments, were performed to complete previous studies involving methanol, ethanol and phenol.

LDI experiments were performed with mixtures of  $\text{Fe}_3\text{O}_4$  with Pr, Sm, Gd, Dy, Yb, Th and U oxides to produce mixed f-d bimetallic oxide cations in the gas-phase and to study their reactivity with hydrocarbons.

Uranium speciation studies in aqueous solutions were continued, using ESI and LDI-FT-ICR/MS, and evidence was obtained for the formation of uranyl perchlorate species [1].<sup>2</sup>

### Communication

[1] Pires de Matos, A., Marçalo, J., Freitas, M. A., Marshall, A. G., Choppin, G. R., Uranium Speciation Studies in Aqueous Solutions by FTICR Mass Spectrometry: Evidence for Uranyl Perchlorate Species, *15th International Mass Spectrometry Conference*, Barcelona, Spain, August 2000.

### Further work

We intend to explore the gas phase ion chemistry of the lanthanide and actinide elements in systems which are progressively closer to condensed phases, namely clusters and coordination/organometallic complexes, trying to get more information about the mechanisms of chemical processes occurring in solution and on solid/gas interfaces. The use of ESI will be pursued to access less stable lanthanide and actinide complex species and to study their gas phase chemistry, and also to develop methods for uranium speciation in aqueous phase.

In the case of the actinides, we will also expand the work, until now limited to Th and U, to the more radioactive members of the series, and perform gas phase ion chemistry studies with Np, Pu, Am and if possible Ac, Pa and Cm, trying to gain insight on a potential 5f electron contribution to chemical reactivity (work to be supported by the POCTI Programme of FCT; approved June 2000, starting January 2001).

<sup>1</sup> Work in collaboration with A.G. Marshall and M.A. Freitas, Department of Chemistry, University of California-Irvine, Irvine, California.

<sup>2</sup> Work in collaboration with W.J. Evans, National High Magnetic Field Laboratory, Tallahassee, Florida.

