The activities of the group comprise the synthesis, characterisation 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.

Relevant facilities maintained in the group are the Fourier transform ion cyclotron resonance mass spectrometer (FT/ICR), a laboratory for catalytic studies including work with CO, a laboratory for calorimetric studies and a laboratory for handling macroscopic quantities of the most toxic actinides. We are starting to apply our knowledge to environmental studies, particularly concerning radioactive waste containing actinides. Of interest to this activity is an ongoing collaboration project with Plastval/Sociedade Ponto Verde dealing with non-radioactive waste.

The work made during 2003 is summarized as follows:

Previous studies on the chemistry of lanthanide compounds with the hydrotris(3,5-dimethylpyrazolyl)borate ligand has been extended to the analogous uranium(III) compound, U(TpMe2)2I, looking for eventual differences between the samarium and uranium chemistry that could reflect differences in accessible oxidation states and in metal-ligand bond polarity. A new ligand framework has been introduced in the context of uranium chemistry, the tacn based ligand. This ligand provides an unusual prismatic coordination environment for the uranium (III) ion leaving an apical position free for electron transfer events. The reactivity of [U((SiMe3NPh)3-tacn)] towards alkyl halides and unsaturated substrates as well as of uranium (IV) complexes [U((SiMe3NPh)3-tacn)X] has been explored. Specially relevant is the observation that [U((SiMe3NPh)3-tacn)NEt3] reacts with methylcyanide to give [U((SiMe3NPh)3-tacn)(Me2(C2N2)C(CN))] as a result of the trimerization of the methylcyanide. Studies of the extraction of the uranium and lanthanide ions with a new ligand resistant to hydrolysis, (CH3NPh)3-tacn, are in progress.

Divalent and trivalent complexes of ytterbium and samarium with 2,6-diterbuthyl-4-methylphenol were immobilised on silica. Solid state 29Si and 13C NMR spectra showed the same final oxidation state for all the metals (+3) and that immobilisation of the organolanthanides occurred.

Pursuing previous work on the study of LnCu2 (Ln = La, Ce, Pr, Nd, Eu, Gd, Dy, Tm, Yb) intermetallic compounds as catalyst precursors, an oxidation-reduction cycle was optimized providing a new method for the synthesis of copper supported catalysts described as CuO particles supported on CeO2 or lanthanide cuprates, Ln2CuO4 or Ln2Cu2O5, which lead to Cu supported on CeO1.5 or Ln2O3 after reduction. This method was also applied to binary actinide intermetallic compounds, ThCu2 and AnNi2 (An = Th, U), leading to 2MO.ThO2 (M = Cu, Ni) and 2CuO.UO3. All these heterobimetallic oxide systems exhibited selectivities in 2-propanol oxidative decomposition.

To enlarge the existing database of alkaline and alkaline-earth metal compounds that allow to predict, with a high precision, enthalpies of formation for new metal alkoxides, additional enthalpies of formation of alkaline metal alkoxides and phenoxides were studied. The enthalpies of formation of new compounds of alkaline metals substituted phenoxides were measured. Gas-phase ion chemistry studies of transuranium actinides by FTICR/MS have continued, with a focus on reactions of An2+ (An = Th, U, Np, Pu, Am) with several oxidants (N2O, H2O, O2, CO2, C2H4O, CH2O, NO), in which we were able to observe for the first time the “bare” neptunyl (NpO22+) and plutonyl (PuO22+) ions, as well as estimate unknown An2+-O and OAn2+-O bond dissociation energies and AnO2+ ionisation energies.

As part of a project on vitrification of radioactive waste, LA-FTICR/MS was used to study several glasses synthesized in our laboratories. Both positive and negative ion spectra were characteristic of the different types of glasses used.

An important part of the output of the Group has been the training of young research students. Some of the group members have been involved in undergraduate and post-graduate university courses. Joint projects with the Faculty of Fine Arts of the University of Lisbon on new lanthanide based fluorescent glasses and with the Glass Museum of Marinha Grande on provenance studies of Portuguese glasses continued. The work made was financially supported by four projects of FCT, one project supported by an industrial association, SPV, two BIIC FCT grants and three FCT PhD grants. Two new projects were approved by FCT.

António Pires de Matos
Research Team

Researchers
- A. PIRES DE MATOS, Coord. Researcher (Group Leader)
- A. DOMINGOS, Princ. Researcher (retired in August)
- N. MARQUES, Principal Researcher
- J. MARÇALO, Auxiliary Researcher
- J. BRANCO, Auxiliary Researcher
- J. P. LEAL, Auxiliary Researcher
- T. A. GASCHE, Auxiliary Researcher
- J. M. CARRETAS, Auxiliary Researcher

Students
- A. S. DIAS, BIIC grantee
- C. HIPÓLITO, PhD student, FCT grant
- C. DIAS, BIIC grantee, POCTI
- M.A. ANTUNES, PhD student, FCT grant
- M. SANTOS, PhD student, FCT grant

Technical Personnel
- A. CARVALHO
- A. J. SOARES

Funding (€)
Research Projects: 78,038,70
Services: 288,65
Total: 78,327,35

Publications
Journals: 6 and 5 in press*
Proceedings: 2
Conf. Communications: 21
Other publications: 2

* One member of the Group, Angela Domingos, contributed as crystallographer to another 5 published papers and 1 in press from the Inorganic and Radiopharmaceutical Chemistry Group of the Chemistry Department of ITN.
Organo-f-Element Chemistry with Multidentate Nitrogen Ligands

M.A. Antunes, B. Monteiro, Dmitrii Roitershtein, A. Domingos, N. Marques

Objectives

This project aims to develop new coordination environments for f-elements with two main purposes:
1. To create new reactive centres with unusual reactivity patterns
2. To use new ligands that can be relevant for An/Ln separation.

These two areas are supported by the projects POCTI/QUI/36015/2000, POCTI/QUI/46202/2002 and POCTI/QUI/46179/2002.

Results

1. We have been exploring the chemistry of lanthanide compounds with the hydrotris(3,5-dimethylpyrazolyl)borate ligand and we have reported the synthesis of a large range of compounds based on the system Sm(TpMe2)2X [1-3].

Now we extended these studies to uranium(III) and we verified that U(TpMe2)2I is a useful precursor for a range of trivalent uranium chemistry [4,5]. We intend to look for eventual differences between the samarium and uranium chemistry that could reflect differences in accessible oxidation states and in metal-ligand bond polarity.

2. Recently we have reported the synthesis and characterization of the uranium(III) complex [U{(SiMe2NPh)3-tacn}] [6]. The ligand (SiMe2NPh)3-tacn generates a trigonal prismatic coordination environment for the metal centre leaving the basal capping position of the trigonal prism available for electron transfer events. [U{(SiMe2NPh)3-tacn}] is easily oxidized with benzyl chloride or I2 to give [U{(SiMe2NPh)3-tacn}X] (X = Cl, I) complexes.

The reactivity of [U{(SiMe2NPh)3-tacn}] is being explored as well as the reactivity of the [U{(SiMe2NPh)3-tacn}X] precursors.

Studies of the extraction of the uranium and lanthanum ions with a new ligand resistant to hydrolysis, (CH2NPh)3-tacn, are in progress.

Published, accepted or in press work


1 Department of chemistry and biology, Moscow City Pedagogical University
**Gas-Phase Ion Chemistry of Lanthanides and Actinides**

J. Marçalo, A. Pires de Matos, J.P. Leal, J.M. Carretas, M. Santos¹, J.K. Gibson², R.G. Haire²

**Objectives**

We have been studying the gas-phase reactivity with organic and inorganic molecules of ions deriving from the metals, metal oxides, metal oxide clusters, intermetallic and organometallic compounds of the lanthanide (Ln) and actinide (An) series elements, as a contribution to a better understanding of the chemistry of these elements. The experimental work is based on the use of Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS), a technique that is specially suited for the study of the chemistry of ion/molecule systems in the gas phase.

Special attention is given to the kinetics, mechanisms and energetics of the reactions, that we try to correlate with the electronic structure of the ions and to compare with analogous processes occurring in solution and on solid/gas interfaces. In the case of the actinides, we intend to gain a better insight into the potential 5f electron contribution to reactivity in the first half of the An series, and to estimate energetic data for An species that may be of interest for condensed-phase processes.

**Results**

We have recently made in our laboratories the first FTICR-MS studies of the gas-phase ion chemistry of the transuranium actinides Np, Pu, and Am [1,2]. We studied the reactions of An⁺ and AnO⁺ (An = Th, U, Np, Pu, Am) with several oxidants which allowed us to estimate unknown An⁻-O and OAn⁻-O bond dissociation energies and to verify literature values obtained by other methods. By means of electron-transfer “branching” experiments with AnO⁺ ions, using amines with well-known ionization energies (IE), it was possible to determine values for IE(AnO⁻) in the cases of Pu and Am. This part of the work has now been extended to the determination of IE(NpO₂⁻) = 6.33±0.18 eV, about 0.6 eV higher than the literature value but in agreement with other thermodynamic data. From the study of the reactions of AnO⁻ with dienes and using a model developed by H. Schwarz and co-workers, the lanthanides, it was possible to determine IE(PuO) and IE(AmO). The results of this study have now started to be revised as a consequence of recent accurate determinations of IE(AnO) for Th and U by M. Heaven and co-workers, which are ca. 0.3 eV higher than the literature values that we used to “anchor” the IE values determined for Pu and Am.

In the sequence of this work and of a previous study with uranium [H. H. Cornehl, C. Heinemann, J. Marçalo, A. Pires de Matos, H. Schwarz, The “Bare” Uranyl (2+) Ion, UO₂⁺²⁺, Angew. Chem. Int. Ed. Engl. 35 (1996) 891-894], we have also studied the reactions of An²⁺ and AnO³⁺ (An = Th, U, Np, Pu, Am) with several oxidants (N₂O, H₂O, O₂, CO₂, C₂H₄O, CH₂O, NO), in which we were able to observe for the first time the “bare” neptunyl (NpO₂⁺²⁺) and plutonyl (PuO₂⁺²⁺) ions, as well as estimate unknown An²⁻-O and OAn²⁻-O bond dissociation energies [3]. We have also studied electron-transfer reactions of AnO₂⁺ (An = Th, U, Np, Pu) and AnO₂⁺²⁺ (An = U, Np, Pu) ions, that allowed us to estimate the second ionization energies of AnO and AnO₂⁺ species [3]. For these estimates we performed an adaptation of the descriptive model of electron-transfer reactions involving doubly charged ions.

We also continued to perform experiments aimed at a comparative study of the gas-phase reactivity of An ions with different organic molecules along the first half of the An series. Previous studies of Th, U, Np, Pu and Am metal and metal oxide cations with indene [4] have been pursued with experiments involving An⁺ and An²⁺ ions and alkanes (methane, ethane, propane, n-butane) and alkenes (ethylene, propene, 1-butene). The lanthanide series cations constitute a key comparison for the actinides and, therefore, following previous studies with Ln⁺ ions and organic molecules [5], experiments involving Ln²⁺ ions and alkanes and alkenes have also been initiated.

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¹PhD grantee (FCT/SFRH/BD/10465/2002). ²Oak Ridge National Laboratory, Oak Ridge, Tennessee.
f-Block Element Intermetallic Compounds as Catalysts Precursors

C. J. Dias, J. Branco, T. A. Gasche, A.P. Gonçalves, A. Pires de Matos

Objectives

New methods for the preparation of supported metal catalysts are of great interest. Intermetallic compounds of lanthanide or actinide metals combined with d metals have been found to be active in a variety of reactions; however the starting compounds decompose under the reaction conditions. The main objective of this project is to study binary copper- or nickel/f block element as catalysts or catalytic precursors.

Results

Pursuing previous work on the study of LnCu₂ (Ln = La, Ce, Pr, Nd, Eu, Gd, Dy, Tm, Yb) as catalytic precursors, an oxidation-reduction cycle was optimized providing a new method for the synthesis of copper supported catalysts:

\[
\begin{align*}
\text{Ln}_2\text{CuO}_4 & \xrightarrow{\Delta (1000 \text{ K/min})} \text{3CuO.Ln}_2\text{CuO}_4 \\
\text{Ln} = \text{La, Ce, Pr, Nd, Eu, Gd} \text{, Dy, Tm, Yb} & \quad \text{CeO}_2, \text{La}_{2}\text{CuO}_4, \text{Nd}_{2}\text{CuO}_4 \quad \text{ThO}_2, \text{UO}_3 \\
\text{Ce}_2\text{CuO}_4 & \xrightarrow{\Delta (1000 \text{ K/min})} \text{3CuO.Ln}_2\text{CuO}_4 \\
\text{Ln} = \text{La, Ce, Pr, Nd, Eu, Gd} \text{, Dy, Tm, Yb} & \quad \text{CeO}_2, \text{La}_{2}\text{CuO}_4, \text{Nd}_{2}\text{CuO}_4 \quad \text{ThO}_2, \text{UO}_3
\end{align*}
\]

Their characterization was done by XRD, TG and TPR. The heterobimetallic copper-lanthanide oxides obtained are described as CuO particles supported on CeO₂ or lanthanide cuprates, Ln₂CuO₄ or Ln₂Cu₂O₅, which lead to Cu supported on CeO₁.₅ or Ln₂O₃ after reduction. To our knowledge, this is the first systematic study on this subject.

The binary actinide intermetallic compounds ThCu₂ and AnNi₂ (An=Th, U) were also used as actinide heterobimetallic oxides (U, Th) precursors leading to 2MO.ThO₂ (M=Cu, Ni) and 2CuO.UO₃ (Fig. 1).

All the heterobimetallic oxides exhibited selectivities in 2-propanol oxidative decomposition, very different from those of pure CuO or lanthanide oxides (Ln₂O₃), which were associated with the f-block element (Fig. 2).

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1 Solid State Group, Chemistry Department, ITN
Synthesis, Characterization and Reactivity Studies of Rare Earth Alkoxides and Aryloxides

Ana S. Dias, José Manuel Carretas, Carla Hipólito, Joaquim Branco, Teresa A. Gasche, João Paulo Leal, Joaquim Marçalo, António Pires de Matos, Anabela Valente, João C. Rocha

Objectives
The application of lanthanide alkoxides and aryloxides are diverse, ranging from catalysis to synthesis of high purity oxide materials. During the last years in our laboratories we have been studying the synthesis and reactivity of several lanthanide and actinide alkoxides and aryloxides including some polynuclear species [J.M. Carretas, J. Branco, J. Marçalo, J.C. Waerenborgh, N. Marques, A. Pires de Matos, J. of Alloys and Comp., 275-277 (1998) 841-843; J.M. Carretas, J. Branco, J. Marçalo, P. Isolani, A. Domingos, A. Pires de Matos, J. of Alloys and Comp., 323-324 (2001) 169-172]. The immobilisation of organometallic complexes on solid surfaces such as oxides or metals in order to prepare relatively well-defined surface species acting as highly selective heterogeneous catalysts are of great interest [C. Copéret, M. Chabanas, R.P. Saint-Arroman, J.M. Basset, Angew. Chem. Int. Ed., 42 (2003) 156]. Recently we started to immobilise our aryloxides on oxide matrices. As a model, the synthesis and characterisation of alkaline and alkaline earth aryloxides was undertaken.

Results
Following previous work on lanthanide aryloxides (1,2) reactions involving phenols containing supplementary donor functions, namely 2,6-dimethoxyphenol and 2-amino-p-cresol, were studied by dissolution of the metals in liquid ammonia, yielding compounds formulated as Eu(OR)₂ and Yb(OR)₃. Substituted aryloxides with alkaline metals (Li-Cs) were also synthesised (3). Divalent and trivalent complexes of ytterbium and samarium with 2,6-diterbutyl-4-methylphenol were immobilised on silica (500). Solid state ²⁹Si and ¹³C NMR spectra showed the same final oxidation state for all the metals (+3) and that immobilisation of the organolanthanides occurred (+4-6). The immobilisation study will be continued in other matrices.

The organolanthanides were characterised by ¹H-NMR, IR, elementar analysis and single crystal x-ray diffraction studies. Solid state ²⁹Si and ¹³C NMR, and thermoanalytic techniques (TGA, DSC) were used additionally for the immobilisation studies.

Published, accepted or in press work

1 Chem. Dep., Aveiro Univ.
Molecular Energetics

J. P. Leal, N. Marques, M. A. Antunes¹, C. Hipólito¹, T. Fernandez²

Objectives
The main objective of the project is to foster the knowledge on energetics of molecules (both inorganic and organic compounds). Special attention is given to f-element compounds. In our laboratories lanthanide and actinide (organometallic and intermetallic), alkaline and alkaline-earth compounds (alkoxides, phenoxides, thiolates and cyclopentadienyls) and hydrocarbons were studied.

Results
To enlarge the existing database of alkaline and alkaline-earth metal compounds that allow to predict, with a high precision, enthalpies of formation for new metal alkoxides, additional enthalpies of formation of lithium, sodium, potassium, rubidium and caesium alkoxides and phenoxides were studied [1-2]. Also, new compounds of alkaline metals with substituted phenoxides were synthesised and their enthalpies of formation measured. The new values fit quite well on a previously developed model [J.P. Leal, J.A. Martinho Simões, J. Organomet. Chem. 460 (1993) 131] proposed to estimate the enthalpies of formation of alkoxide species via their lattice enthalpies. A compilation of existing enthalpies of formation for hydrocarbons was made. Those values were used to parametrize and extend the Laidler method of additive contributions. The newly parametrized method allows to estimate the enthalpy of formation (gas and condensed phase) for virtually any hydrocarbon. For the first time, physical meaning was associated to the parameters (see Figure), leading to a deeper understanding of bond energetics on these compounds. A publication on this subject will be ready in the beginning of 2004.

A solid state thermal bath conduction calorimeter (conceived and designed in our group) was set up. This calorimeter allows simultaneous thermal and gas chromatography analysis over the same sample.

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8. C. Hipolito, J. P. Leal, Standard Enthalpies of Formation of Substituted Alkaline Metal Phenols, 6º Encontro Nacional de Química-Física, SPQ, Lisboa, Portugal, Agosto-Setembro de 2003

¹ PhD. Student, FCT grant.
² Departamento de Química e Bioquímica, FC-UL.
Glass Science with Applications in Radioactive Waste Vitrification and Art Studies

A. Pires de Matos, J. Marçalo, M. Santos, F. Araújo, P. Valério

Objectives

The main objective of this project is to develop in ITN know how in glass science to contribute to the research on radioactive waste vitrification processes. The study of old glasses and their weathering is also important as the corrosion mechanisms which lead to their alteration concerns the waste disposal.

For structural information the main technique we are using is laser ablation Fourier transform ion cyclotron resonance mass spectrometry (LA-FTICR/MS) trying to correlate the gas phase clusters formed with the basic structure of the glass. As we are developing expertise on glass science, particularly in the synthesis and characterization of glasses, two other applications were envisaged in collaboration with university research groups: one concerns the development of new glasses for art applications, the other involves provenance studies of Portuguese glass from the 15th to the 20th century.

Results

a) UV (221.67nm) and IR (1064nm) LA-FTICR/MS was used to characterize several types of glass. Following previous work made in our laboratories (M. Santos, J. Marçalo, A. Pires de Matos, Characterization of Glasses by FTICR Mass Spectrometry, Phys. Chem. Glasses 43C (2002) 421-423), a tentative correlation between positive ion distribution and glass elemental composition was made and ions of the major constituents like Si⁺, Na⁺, K⁺, Ca⁺, Al⁺, and Pb⁺ had rather strong abundances. Negative ion spectra were made in order to find if a correlation between the types of glasses and the negative ion clusters obtained could be established. Besides the ions BO₂⁻, SiO₂⁻, SiO₃⁻, PO₃⁻, several types of clusters were observed, namely (SiO₂)ₓ(SiO₂)ᵧ, (SiO₂)ₓ(X=O, OH, AlO₂, AlO, KO, NaO, FeO₂, …) and also (SiO₂)ₓBO₂⁻, (SiO₂)ₓ(B₂O₃)ₓNaO⁻, etc.. The relative abundance of these ions was characteristic of the type of glass analysed. This work was made in collaboration with J. F. Muller of the University of Metz, where the experiments with UV laser were made, and part of it was included in a PhD thesis of a student, Eric Erel, from the University of Metz.

b) Ruby goblets from Marinha Grande and Oliveira de Azeméis, were studied using X-ray fluorescence, FTICR/MS and electronic absorption spectroscopy. The colours in the different goblets were due either to the presence of gold or to a semiconductor cromophor, containing Se, S and Cd. FTICR/MS of a based Cd industrial pigment was studied, as well as the positive and negative ion spectra of CdS, CdSe and CdTe synthesized in our laboratories.

c) New fluorescent glasses containing europium, samarium, terbium, cerium and uranium were synthesized using a sodocalcium-silicate glass or an industrial glass with a known formulation from Jasmim Glass Factory in Marinha Grande. This work involves researchers from the Faculty of Fine Arts of the University of Lisbon and from the University of S. Paulo, Brasil.

d) Concerning the work on provenance studies of Portuguese Glass (1,2), which is being made in collaboration with the Glass Museum of Marinha Grande, the University of Antwerp and the Polytechnical Institute of Tomar, preliminary analytical results were obtained from samples from Marinha Grande and other locations. Both sodium and potassium based glasses were found.

Published, accepted or in press work


1 PhD grantee (FCT/SFRH/BD/10465/2002).
2 Environmental Analytical Chemistry Group, Chemistry Department, ITN.