

## Uranium Chemistry with Multidentate Nitrogen Ligands

M.A. Antunes, M. Dias, A. Domingos, I.C. Santos, 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. Studies on the reactivity of  $U(Tp^{Me_2})_2I$  were pursued. Salt metathesis of  $U(Tp^{Me_2})_2I$  and/or acid-base reactions of amidouranium precursors showed to be an entry into an extensive family of uranium(III) compounds [1-3].

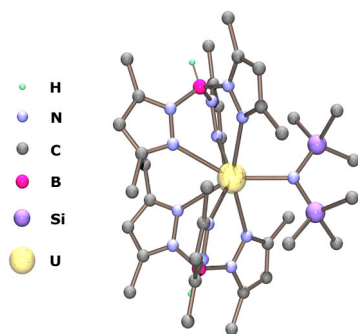


Diagram of  $[U(Tp^{Me_2})_2\{N(SiMe_3)_2\}]$

2. The reactivity of  $[U\{(SiMe_2NPh)_3-tacn\}]$  is being explored and may be illustrated by their mediation of the following selected reactions: 1) the formation of complex heterocycles from the reduction of various organic substrates 2) reductive cleavage of S-S and S-P bonds 3) oxidation by silver halides or TI salts of cyclopentadienyls or phosphoryls. The reactivity of the uranium(IV) amido complexes,  $[U\{(SiMe_2NPh)_3-tacn\}(NR_2)]$ , towards protic substrates and small dipolar molecules is also being studied [4-6].

3. Studies on the synthesis of dianionic, mixed Cp/Bpz continued. The new ligand  $K_2[PhB(3-Mepz)_2(C_5Me_4)]$  has been synthesized and the result of the interaction of this ligand with lanthanide and uranium halides is under study [7].

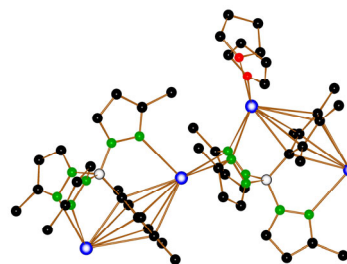


Diagram of  $[K_2(THF)_2B(3-Mepz)_3(C_5Me_4)]_{\infty}$

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4. N. Marques, “*f*-Element Chemistry with functionalised TACN Ligands”, *XXXVI International Conference on Inorganic Chemistry*, Mérida, Mexico, 2004, invited lecture.
5. M. A. Antunes, B. Monteiro, A. Carvalho, J. P. Leal, I. C. Santos, Â. Domingos, N. Marques, Novos Complexos de Urânio com o Ligando  $\{(SiMe_2NPh)_3-tacn\}$ , *XIX Encontro Nacional da Soc. Portuguesa de Química*, Coimbra, 2004.
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## Gas-Phase Ion Chemistry of Lanthanides and Actinides

J. Marçalo, A. Pires de Matos, J.P. Leal, M. Santos, John K. Gibson<sup>1</sup>, Richard G. Haire<sup>1</sup>

### Objectives

As a contribution to a better understanding of the chemistry of the lanthanide (Ln) and actinide (An) series elements, we have been studying the gas-phase reactivity of “bare” and ligated ions of these elements with organic and inorganic molecules. 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. We obtain information on 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 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 thermodynamic data for An species that may be of interest for condensed-phase processes.

### Results

**1. Gas-phase thermochemical studies of An oxides [1-4].** We pursued studies of the gas-phase chemistry of atomic and oxygen-ligated positive and dipositive An ions (An = Th, U, Np, Pu, Am). Oxidation and electron-transfer reactions allowed us to derive bond energies, enthalpies of formation and ionization energies for the neutral and ionic monoxides and dioxides. We verified that the “bare” actinyls  $\text{UO}_2^{2+}$ ,  $\text{NpO}_2^{2+}$  and  $\text{PuO}_2^{2+}$  are thermodynamically stable towards Coulomb dissociation and we were able to predict that the non-observed “bare”  $\text{AmO}_2^{2+}$  is also stable. The first and second ionization energies of the An monoxides and dioxides were assessed: comparisons were made with literature values and with the ionization energies of An atoms and of relevant molecules. The gas-phase results in conjunction with the known aqueous thermochemistry of the actinyls allowed us to derive hydration enthalpies for the  $\text{AnO}_2^{2+}$  (An = U, Np, Pu, Am), that we found to be essentially the same for these four An but substantially more negative than previously reported ones. This work was extended to Pa, in what constituted the first FTICR/MS studies of the gas-phase ion chemistry of this element. Preliminary experiments demonstrated that “bare”  $\text{PaO}_2^+$  is a very stable species, reflected in a  $\text{OPa}^+\text{-O}$  bond energy larger than that for the analogous U species, and in an ionization energy higher than those for the Np and Pu dioxide cations. Another preliminary result of interest was the observation of “bare” protactinyl,  $\text{PaO}_2^{2+}$ , formally a Pa(VI) species.

**2. Comparative studies of the gas-phase reactivity of An cations with organic molecules [5].** We continued our studies of the gas-phase reactivity of An ions with organic molecules. Experiments involving  $\text{An}^+$  and  $\text{An}^{2+}$  ions (An = Th, Pa, U, Np, Pu, Am) and alkanes and alkenes were completed. The recent addition of Pa to these studies allowed us to draw more definitive conclusions on the relative reactivity of An cations in the first half of the series. Experiments involving the doubly-charged Ln series cations, as key An analogues, were concluded. Experiments with  $\text{Ta}^+$  and  $\text{Ta}^{2+}$  were also performed, to check for group 5 type behaviour of Pa. The results are being interpreted in the context of the electronic structures and energetics of the An and the other elements studied.

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4. J. K. Gibson, R. G. Haire, J. Marçalo, M. Santos, A. Pires de Matos, J. P. Leal, Thermodynamic Properties of Actinide Oxide Molecules from Gas-Phase Ion Chemistry, *11th Symposium on Thermodynamics of Nuclear Materials*, Karlsruhe, Germany, September 2004.
5. M. Santos, J. Marçalo, A. Pires de Matos, J. K. Gibson, R. G. Haire, Probing the Participation of 5f Electrons in Gas-Phase Reactions of Actinide Cations with Small Alkanes and Alkenes, *34ièmes Journées des Actinides*, Heidelberg, Germany, April 2004.

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## Oxidative Coupling of Methane Using Binary Actinide (Th, U) Intermetallic Compounds as Catalytic Precursors

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### Objectives

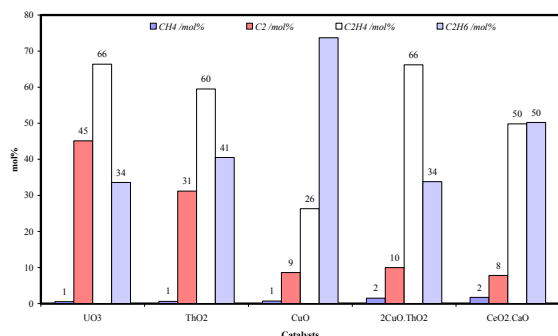
The study of the oxidative coupling of methane using binary actinide intermetallic compounds, AnNi<sub>2</sub> (An=Th, U) and ThCu<sub>2</sub>, as catalytic precursors is the main goal of this work. Ethylene and ethane are the target and strategic C<sub>2</sub> products.



### Results

Heterobimetallic An-Ni-O (An=Th, U) and Th-Cu-O oxides were obtained after controlled oxidation of binary actinide intermetallic compounds, AnNi<sub>2</sub> (An=Th, U) and ThCu<sub>2</sub>. They were used for the first time as catalysts for the oxidative coupling of methane using carbon dioxide instead of O<sub>2</sub> as the oxidant agent.

The results obtained were compared to those of pure oxides, including CeO<sub>2</sub>-CaO, Fig. 1.



With CO<sub>2</sub>, the behaviour of ThO<sub>2</sub>, UO<sub>3</sub> and 2CuO.ThO<sub>2</sub> is very similar, with C<sub>2</sub> yields and C<sub>2</sub>H<sub>4</sub> selectivities higher than those of CeO<sub>2</sub>-CaO. Moreover, nickel based catalysts present the highest activities (50 – 70%) but the only products are CO<sub>x</sub>. Correlation between CuO, ThO<sub>2</sub> and 2CuO.ThO<sub>2</sub> behaviour shows a Strong Metal Support Influence (SMSI) attributed to thorium oxide.

With O<sub>2</sub>, the selectivity for C<sub>2</sub>H<sub>4</sub> increases until 75-80%, whereas the C<sub>2</sub> yield decreases for ThO<sub>2</sub> and UO<sub>3</sub> (25 %)

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2. J. Branco, D. Ballivet-Tkatchenko, A. Pires de Matos, Reduction of Heterobimetallic Copper-Lanthanide Oxides, *Thermochim. Acta*, in press.

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## Synthesis, Characterization and Reactivity Studies of Rare Earth Alkoxides and Aryloxides

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### Objectives

During the last years in our laboratories we have been studying the synthesis and reactivity of several lanthanide and actinide alkoxides and aryloxides. Lanthanide alkoxides and aryloxides have a wide range of applications from catalysis to synthesis of high purity oxide materials. The main goals of this project are: 1) the synthesis of well characterized alkoxides and aryloxides of lanthanide metals, and also alkaline and alkaline-earth metals that can be used as models for lanthanide compounds; 2) the synthesis of heterometallic alkoxides and aryloxides and preparation of supported homo- and heterometallic alkoxides; 3) applications as inorganic precursors of well characterized heterometallic oxides; 4) catalytic studies using valuable molecules such as  $\text{CO}_2$  and  $\text{CH}_4$ .

### Results

Alkaline and alkaline-earth metal alkoxides are very good models for rare-earth alkoxides, but easier of synthesizing. Some of the rare-earth alkoxides (Sc, Y, La) are easily comparable with their neighbors in the periodic table (Ca and K, Sr and Rb, Ba and Cs, respectively). In order to explore new patterns and to achieve a deeper insight on rare-earth alkoxides, alkaline and alkaline-earth metal substituted phenoxides were synthesized. Different positions of the substituents and also different substituents were used. Their characterization, both energetically and structurally was performed [C. Hipólito, J. P. Leal, Standard Molar Enthalpies of Formation of Li, Na, K, Rb and Cs Methylphenoxides, *Thermochim. Acta* (submitted); C. Hipólito, J. P. Leal, Standard Molar Enthalpies of Formation of Alkaline Earth Phenoxides, *Inorg. Chim. Acta* (submitted)].

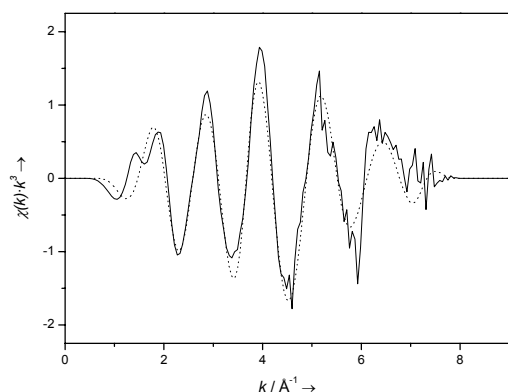


Fig. 1. EXAFS spectrum of  $\text{Cs}[\text{O}(2,6\text{-t-Bu}_2\text{Ph})]_2$

On what concerns the energetic, the measurement of the enthalpies of formation of the phenoxides was done using an isoperibol reaction-solution calorimeter. For the structural characterization powder X-ray and EXAFS were used. Also some correlation between energetic and structural data was attempted [C. Hipólito, J. P. Leal, Standard Molar Enthalpies of Formation of Alkaline Earth Phenoxides, *Inorg. Chim. Acta* (submitted)].

Following previous work on lanthanide alkoxide chemistry [1], the reactions of samarium, europium and ytterbium involving ketones, namely acetone and 3-pentanone, were studied by dissolution of the metals in liquid ammonia and by metal vapour synthesis, yielding aldolate compounds rather than simple alkoxides.

Preliminary results show that lanthanide heterometallic alkoxides can be synthesized using the metal vapour synthesis technique and the dissolution of the metals (Sm, Eu, Yb, Ca, Ba) in liquid ammonia together with ethanol and 2-propanol. Eu-Ca or -Ba alkoxides were used as molecular inorganic precursors of heterometallic oxides. Studies of temperature programmed oxidation (TG and TPO) allowed the optimization of the experimental conditions for their decomposition. They were characterized by X-ray diffraction (powder) and temperature programmed reduction (TG and TPR). Eu-Ca-O was used on the oxidative coupling of methane (OCM), using  $\text{CO}_2$  an oxidant agent. The preliminary results obtained are very promising with  $\text{C}_2$  yield (70%) and  $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$  selectivities (30:70%) close to those reported for  $\text{CeO}_2/\text{CaO}$  (85 and 20:80%, respectively), the best catalyst reported so far for this reaction.

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## Molecular Energetics of Organic, Inorganic and Organometallic Compounds

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### Objectives

The main objective of this project is to collect data and rationalize it in a systematic way that enables a deeper knowledge of energetics on molecules (both inorganic and organic compounds). Special importance will be given to f-element compounds (both in the solid state and in solution). To achieve this goal, 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 and phenoxides, additional enthalpies of formation of alkaline and alkaline-earth metal substituted phenoxides were studied [1]. The new values fit quite well on a previously developed model (J. P. Leal, J.A. Martinho Simões, *J. Organomet. Chem.* **1993**, *460*, 131-138; P. Nunes, J. P. Leal, V. Cachata, H. Raminhos, M. E. Minas da Piedade, *Chem. Eur. J.* **2003**, *9*, 2095-2101) proposed to estimate the enthalpies of formation of alkoxide species *via* their lattice enthalpies. The thermochemical studies with lanthanide phenoxides already began and results are expected next year. These studies will allow the reliable prediction of enthalpy of formation values for the lanthanide alkoxide family.

Strange and erroneous values in the literature of the formation enthalpies, and state change enthalpies, of cresols lead to an extremely careful purification of these compounds and to the re-determination of the values under suspicion. Some of the wrong ones were already identified and a coherent set of values will be available in two or three months.

The gas-phase acidity of substituted phenols (a key value for the knowledge of O-H bond strength) was determined by several different methods using the FT-ICR mass spectrometer facility. Those values are determinant to the evaluation of anti-oxidant properties of substituted phenols (e.g. Vitamin-E derived compounds).

A critically accessed compilation of existing enthalpies of formation for hydrocarbons was finished and those values were used to parametrize an extended 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, leading to a deeper understanding of bond energetics in these compounds [J. P. Leal, Additive methods for prediction of thermochemical properties. The Laidler method revisited. 1. Hydrocarbons, *J. Phys. Chem. Ref. Data* (submitted)]. This compilation also leads to a database called "Laidler 2004" which includes more than 240 hydrocarbons and alkyl radicals.

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. The prototype is ready for preliminary tests.

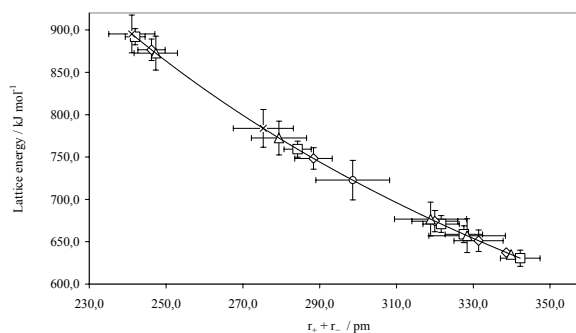


Fig.1 Lattice energy *versus* thermochemical distance. [squares – MOPh, diamond – MO(2-MePh), triangle – MO(2,6-Me<sub>2</sub>Ph), cross – MO(2,4,6-Me<sub>3</sub>Ph), sphere – MO(2,6-*t*-Bu<sub>2</sub>Ph)].

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3. C. Hipólito, J. P. Leal, Standard Molar Enthalpies of Formation of Li, Na, K, Rb and Cs Methylphenoxides, *Thermochim. Acta* (submitted).

<sup>1</sup> Student of DQB Faculdade Ciências Univ. Lisboa

## Glass Science with Applications in Radioactive Waste Vitrification and Art Studies

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### 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

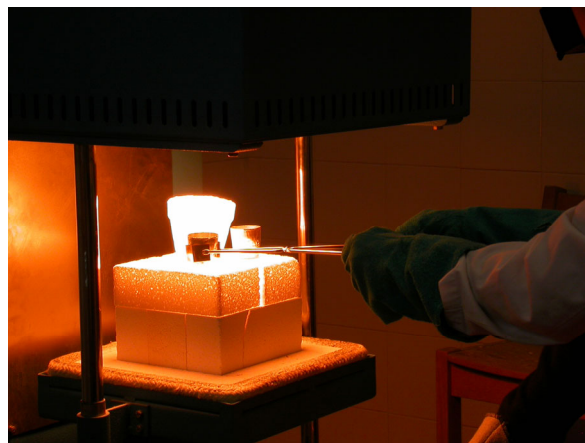
During 2004 the main effort has been in the set-up of a laboratory for glass research, mainly for synthesis and processing of glass materials. This laboratory, which is run by a new research unit, “Vidro e Cerâmica para as Artes”, is supported by the pluriannual programme of the Foundation for Science and Technology (FCT). This infrastructure is the place where interdisciplinary projects of researchers from ITN, from the Department of Conservation and Restoration of the New University of Lisbon (UNL) and from the Faculty of Fine Arts of the University of Lisbon are being held. Analytical instrumentation supporting these projects is either at ITN or at UNL.

Laser ablation coupled with mass spectrometry has been explored in our laboratory to generate and study silicon/oxide and/or silicon/aluminium/oxide negative ion clusters. The variety and the yield of the clusters formed could be a fingerprint to the

solid phases studied [1]. We are also studying the gas phase ratios of metal ion/metal oxide ion obtained by laser ablation to investigate if a different bonding strength could be correlated with the ease or difficulty of lixiviation. Several glass samples have been prepared.

The study on new fluorescent glasses containing lanthanide oxides continued using sodocalcium-silicate glasses prepared in our laboratory or an industrial glass with a known formulation from Jasmim Glass Factory in Marinha Grande. Reduction to Eu(II) was achieved adding to the raw materials SiC. This project results from a collaboration with the Faculty of Arts of the University of Lisbon. A project submitted to FCT was approved for two years.

Concerning the work on provenance studies of Portuguese Glass, which is being made in collaboration with the Glass Museum of Marinha Grande, the New University of Lisbon, the University of Antwerp and the Poly-technical Institute of Tomar, preliminary analytical results were obtained from samples from Marinha Grande and other locations. In order to evaluate the errors obtained in a portable XRF instrument, used for non-destructive analysis, several glass samples of known composition were prepared and analysed. This work should continue in the next two years as a submitted project was approved by FCT.



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