

Inorganic and Organometallic Chemistry

António Pires de Matos

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 structure 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 a Fourier transform ion cyclotron resonance mass spectrometry (FTICR/MS) laboratory, 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. Collaboration is also given to the Radiation Technologies: Processes and Products group (Physics Sector) in a study of the gamma radiation effect on several waste water sources.

Ongoing research to develop new coordination environments for *f*-elements is continuing with two main purposes: to create new reactive centres with unusual reactivity patterns and to explore the ability of the new ligands in Ln/An separation. During the last year we developed protocols for the synthesis of a monoanionic tacn based ligand [(SiMe₂NPh)-tacn(¹Pr)₂] and the dianionic bisalkoxide- and bisdiamide-diamine ligands. Reactivity studies of these ligands with lanthanide halides and uranium triiodide are under investigation.

Pursuing previous work on binary lanthanide (LnCu₂ (Ln = La, Ce, Pr, Nd, Eu, Gd, Dy, Tm, Yb) and actinide (ThCu₂ and AnNi₂; An=Th, U) intermetallic compounds as catalytic precursors, leading to heterobimetallic oxides, 3CuO.Ln₂CuO₄ or 2CuO.Ln₂Cu₂O₅ and 2MO.ThO₂ (M=Cu, Ni) or 2CuO.UO₃, a systematic study of their acid-base properties was undertaken. Two methods were used: 2-propanol dehydrogenation/dehydration and the temperature programmed desorption of CO₂. The results show a correlation between the catalysts basicity and the catalytic activity, which decreases along the lanthanide series. For the actinides uranium oxide behaves better than thorium oxide: stronger and richer basicity together with higher activity and better selectivity for C₂ products (oxidative coupling of methane). These results clearly indicate that the *f*-block element plays a role in the heterobimetallic oxides properties.

Gas-phase ion chemistry studies of highly radioactive actinides by FTICR/MS have been continued. Oxidation studies of monopositive and dipositive actinide ions were pursued, with a focus on Pa and Cm. It was found that PaO₂²⁺, formally a Pa(VI) species, catalyzes the oxidation of CO by N₂O.

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 and the New 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 seven projects of FCT, three FCT PhD grants and one Post-doc FCT grant. A new project approved by FCT will support the installation of an ESI mass spectrometer

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Gas-Phase Ion Chemistry of Actinides and Lanthanides

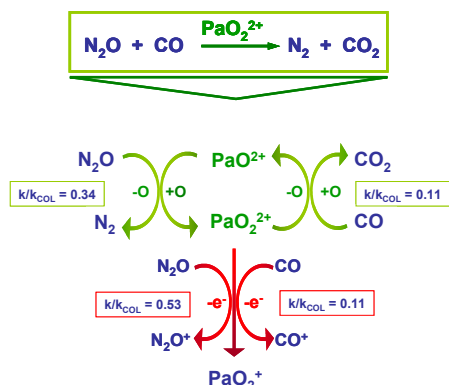
J. Marçalo, A. Pires de Matos, J.P. Leal, M. Santos¹,
J.K. Gibson², R.G. Haire²

Objectives

The gas-phase reactivity of “bare” and ligated actinide and lanthanide ions with organic and inorganic molecules is studied in order to obtain kinetic, mechanistic and energetic information that can be correlated with the electronic structure of the ions and compared with data from condensed phases. For the actinides, the aims are also to gain insight into a potential 5f electron contribution to the chemistry in the first half of the series, and to estimate thermodynamic data for species that may be of interest for condensed-phase processes. 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.

Results

Oxidation studies of monpositive and dipositive actinide ions were pursued [1-4,6], with a focus on Pa and Cm. Reactions of atomic and ligated, monpositive and dipositive Pa ions were studied. Notably, it was observed that PaO^{2+} was oxidized by N_2O to yield PaO_2^{2+} , formally a Pa(VI) species. The experimentally determined $\text{IE}[\text{PaO}_2^+] \approx 16.6$ eV was in agreement with theoretical calculations performed by R. Tyagi and R. M. Pitzer from Ohio State University (Columbus, Ohio, USA). It was found that PaO_2^{2+} catalyzes the oxidation of CO by N_2O (see Scheme); such O atom transport via a dipositive metal oxide ion is distinctive.



Preliminary studies of oxidation reactions of “bare” and ligated, monpositive and dipositive Cm ions were also performed. Oxidation reactions of Gd and Lu ions were examined for comparison.

Comparative studies of the reactivity of actinide and lanthanide cations with organic molecules were continued [3-6]. The reactivity of doubly-charged cations An^{2+} ($\text{An} = \text{Th}, \text{Pa}, \text{U}, \text{Np}, \text{Pu}, \text{Am}, \text{Cm}$) and Ln^{2+} ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{Lu}$) with alkanes and alkenes was examined. The reaction channels observed were

highly dependent on the metal ion and typically consisted of combinations of dehydrogenation and/or alkane-losses with electron, hydride and/or methide transfers. The early actinide cations, Th^{2+} , Pa^{2+} and U^{2+} , were the most reactive; Th^{2+} , in particular, efficiently induced the dehydrogenation of methane, yielding ThCH_2^{2+} as single product. La^{2+} , Gd^{2+} and Lu^{2+} were the most reactive lanthanide cations, but Lu^{2+} , due to its high electron affinity, reacted only via transfer channels.



Published or in press work

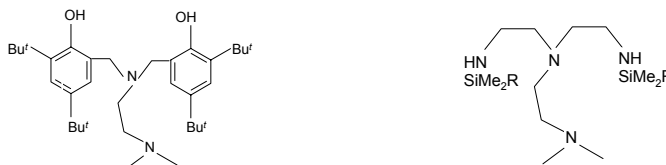
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¹ PhD grantee (FCT/SFRH/BD/10465/2002).

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f-Element Chemistry with Multidentate Nitrogen and Oxygen Donor Ligands*M. A. Antunes, S. Barroso, J. Cui, J. M. Carretas, N. Marques*

This project aims to develop new coordination environments for *f*-elements with two main purposes: to create new reactive centres with unusual reactivity patterns and to explore the ability of the new ligands in Ln/An separation. These two areas are supported by the projects POCTI/QUI/36015/2000, POCTI/QUI/46202/2002 and POCTI/QUI/46179/2002. Studies on the reactivity of $[U(Tp^{Me_2})_2I]$ have been accomplished as well as those based on the U(III) and U(IV) complexes, $[U(\{SiMe_2NPh\}_3-tacn)]$ and $[U(\{SiMe_2NPh\}_3-tacn)X]$ (X = halide and diphenylamide). Now we are involved on the synthesis of mono- and difunctionalized tacn ligands. The synthesis of the monoanionic ($\{SiMe_2NPh\}-tacn(^iPr)_2$) ligand has been achieved, but our efforts to get the dianionic ($\{SiMe_2NPh\}_2-tacn(Me)\}$, failed so far. Hence, we changed our strategy to the synthesis of the new dianionic bisalkoxide and bisamide diamines.



Reactivity studies of these ligands with lanthanide halides and uranium tri-iodide are under active investigation.

Molecular Energetics of Organic, Inorganic and Organometallic Compounds*J. P. Leal, M. T. Fernandez¹, C. Hipólito, P. Madeira², L. Richard³, R. Simões³*

The main objective of this research line 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 on 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.

During 2005 new enthalpies of formation for alkaline-earth metal and lanthanide substituted phenoxides were measured. 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 keystone for 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 and for the first time, a physical meaning was associated to the parameters. New fluoroapatite compounds were synthesized and their thermal and structural properties studied.

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Synthesis, Characterization and Reactivity Studies of Rare Earth Alkoxides and Aryloxides*J. M. Carretas, C. Hipólito, J. Branco, T. Almeida Gasche, J. P. Leal, A. S. Correia, A. Pires de Matos*

Alkaline and alkaline-earth metal alkoxides are very good models for rare-earth alkoxides and easier to synthesize. 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 in these comparisons, alkaline, alkaline-earth and rare-earth substituted phenoxides were synthesized. Different positions of the substituents and also different substituents were used. Their characterization, both energetic and structural, was performed. The measurement of the enthalpies of formation of the phenoxides was made by reaction-solution calorimetry. For the structural characterization powder X-ray and EXAFS were used.

Following previous work on lanthanide heterobimetallic oxides (Eu-M-O, M=Ca, Ba), the study of their acid-base properties was undertaken.

f-Block Element Intermetallic Compounds as Catalysts Precursors*J. Branco, A. Pires de Matos*

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.

Pursuing previous work on binary lanthanide (LnCu_2 ; $\text{Ln} = \text{La, Ce, Pr, Nd, Eu, Gd, Dy, Tm, Yb}$) and actinide (ThCu_2 and AnNi_2 ; $\text{An} = \text{Th, U}$) intermetallic compounds as catalytic precursors, leading to heterobimetallic oxides, $3\text{CuO.Ln}_2\text{CuO}_4$ or $2\text{CuO.Ln}_2\text{Cu}_2\text{O}_5$ and 2MO.ThO_2 ($\text{M} = \text{Cu, Ni}$) or 2CuO.UO_3 , a systematic study of their acid-base properties was undertaken. Two methods were used: 2-propanol dehydrogenation/dehydration and the temperature programmed desorption of CO_2 . The results show a correlation between the catalysts basicity and the catalytic activity, which decreases along the lanthanide series. For the actinides uranium oxide behaves better than thorium oxide: stronger and richer basicity together with higher activity and better selectivity for C_2 products (oxidative coupling of methane). These results clearly indicate that the f-block element plays a role in the heterobimetallic oxides properties.

Immobilized Surface Rare Earth and Actinide Aryloxides. Activation of Small Molecules (CO_2 , CH_4 , C_2H_6)*T. Almeida Gasche, A. S. Correia, J. Branco*

One objective of surface organometallic chemistry is to immobilise organometallic complexes on solid surfaces such as oxides and zeolites to prepare well-defined surface species acting as highly selective heterogeneous catalysts. For several years, we have been studying the synthesis and reactivity of lanthanide and actinide aryloxides. Some divalent and trivalent samarium and ytterbium 2, 6-di-*tert*-butyl-4-methylphenoxo complexes were immobilised on amorphous silica. For the divalent complexes, the results pointed that after reaction with silica only one aryloxide group remains bonded to the metal, with formation of a η^2 type complex involving two Si-OH groups and oxidation of the divalent complexes. In order to obtain additional information on these immobilised systems, the cuboctameric silsesquioxane monosilanol ($(\text{C}_5\text{H}_9)_7\text{Si}_8\text{O}_{12}(\text{OH})$) was used as a homogeneous model system. The silanol mentioned belongs to the polyhedral oligomeric silsesquioxanes family (POSS) which are used to model the surface structure of partially dehydroxilated silica and therefore infer information about the coordination sphere of metal complexes directly supported on silica. During 2005 synthesis of divalent ytterbium and europium 2,6-di-*tert*-butyl-4-methylphenoxo complexes with ($(\text{C}_5\text{H}_9)_7\text{Si}_8\text{O}_{12}(\text{OH})$) was performed. The organolanthanides silanol systems were characterized by NMR, IR, elementary analysis, TGA and DSC. The DSC results showed only exothermic processes. It was also concluded that the Yb-POSS bond is stronger than the Eu-POSS bond. The results obtained so far corroborate the ones obtained for the divalent lanthanide aryloxides after deposition on silica.

Glass Science with Applications in Radioactive Waste Vitrification, Archaeometry and Art Studies*A. Pires de Matos, J. Marçalo, M. Santos, F. Lopes*

We are developing 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. Sodocalciumsilicate glass samples containing several rare earths, uranium and thorium oxides have been synthesized.

As we are developing expertise on glass science, particularly in the synthesis and characterization of glasses, we started collaboration with university research groups supported by two FCT projects: 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. The historical glasses have started to be analysed by XRF spectrometry and by ICP/MS. A series of new luminescent glasses with rare earths have already been prepared.

Gamma Irradiated Chitosan/pHEMA Membranes for Drug Release Systems*M. H. Casimiro, J. P. Leal, M. H. Gil¹*

With the purpose of obtaining a biocompatible and sterilized matrix 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 ^{60}Co source.

From previous work on chemical and physical characterisation, we have selected the most interesting synthesis conditions and done microbiological, biocompatibility and antibiotic release studies on the obtained membranes.

Results point out that membranes naturally exhibit antimicrobial properties and that over the studied range values, drug loaded membranes display an insignificant level of haemolysis and present a fast rate of amoxicillin release. In order to optimise the drug release rate we intend to do further work on membranes thickness.

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