

Inorganic and Organometallic Chemistry

Noémia Marques

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 energetic 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.

Work on uranium chemistry with the nitrogen donor ligands Tp^{Me_2} and $(\{\text{SiMe}_2\text{NPh}\}_3\text{-tacn})$ was completed. The results are included in several publications and are part of a PhD Thesis submitted to Faculdade de Ciências da Universidade de Lisboa. Studies on the reactivity of mono- functionalized tacn ligands and bis(phenolate)diamine ligands are now under investigation. Alkyl derivatives of the complexes based on these two type of ligands, $[\text{MCl}_2\{\text{O}(3,5\text{-}^t\text{Bu}_2\text{Ph})\}\text{-tacn}(\text{Pr}_2)]$ ($\text{M}=\text{Ti}, \text{Y}, \text{Sm}$) and $[\text{MCl}(\text{O}_2\text{-}^t\text{Bu}_2\text{NN})(\text{L})]$ ($\text{M} = \text{Ti}, \text{Y}$) are being tested in the polymerization of olefins.

Gas-phase ion chemistry studies of the actinides ($\text{An} = \text{Th}$ through Cm) by FTICR/MS were continued. The reactions of bare and oxo-ligated An cations with hydrocarbons were investigated and revealed a significant 5f-electron participation in organoactinide bond formation for Pa^+ and PaO^+ . New AnPt^+ species were synthesized and the chemistries of Uir^+ , UPt^+

and UAu^+ examined in the context of the theoretical prediction of strong actinide-transition metal bonds.

Pursuing previous work, we have applied the urea-nitrate combustion method to the synthesis of $\text{BaO-La}_2\text{O}_3$ and MO-CeO_2 ($\text{M} = \text{Ba}, \text{Ca}$) nanoparticles, promising candidate catalytic systems for CO_2 valorization as C1 feedstock, namely through the selective oxidation of methane (OCM reaction).

A collaboration study with Faculdade de Ciências da Universidade de Lisboa and ITQB using the FTICR/MS facility showed that ionic liquids in the gas-phase behave as neutral ion-pairs and proved that it is possible to fractionally distill ionic liquids.

We are also applying our knowledge to environmental studies, particularly in the study of vitrification of radioactive wastes containing actinides and, in collaboration with the Radiation Technologies: Processes and Products group (Physics Sector), in a study of the gamma radiation effect on several waste water sources. Of importance is also a new collaboration with OMNIDEA, Lda., a start-up company dedicated to R&D of aerospace technology and energy systems.

Joint projects with the Faculdade de Belas Artes da Universidade de Lisboa on new lanthanide based fluorescent glasses and with the Glass Museum of Marinha Grande on provenance studies of Portuguese glasses continued.

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. The work made was financially supported by several projects of FCT, four FCT PhD grants and one Post-doc FCT grant. A ESI mass spectrometer was acquired with support of FCT.

Research Team

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f-Element Chemistry with Multidentate Nitrogen and Oxygen Donor Ligands

M. A. Antunes, B. Vieira, J. Cui, J. M. Carretas, A. M. Martins¹, N. Marques

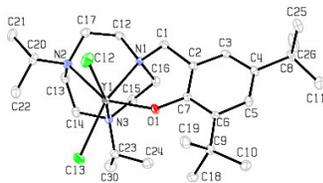
Objectives

This project aims at to develop new coordination environments for *f*-elements with two main purposes: 1. To create new reactive centres with unusual reactivity patterns. 2. To explore the ability of new ligands in An/Ln separation.

Results

Work on uranium chemistry with the nitrogen donor ligands Tp^{Me_2} and $\{(\text{SiMe}_2\text{NPh})_3\text{-tacn}\}$ (POCTI/QUI/46179/2002) was completed [1]. The results are included in several publications and are part of a PhD Thesis submitted to Faculdade de Ciências da Universidade de Lisboa.

Studies on the reactivity of complexes based on mono-functionalized tacn ligands has proceeded (POCTI/QUI/46202/2002). The ligand $\{(\text{SiMe}_2\text{NPh})\text{-tacn}^{(\text{iPr}_2)}\}$ allowed the isolation of $[\text{MCl}_2\{(\text{SiMe}_2\text{NPh})\text{-tacn}^{(\text{iPr}_2)}\}]$ ($\text{M} = \text{Ti}, \text{Y}$), but the system was not further explored since the reactions always gave secondary products due to nucleophilic attack on the Si of the SiMe_2NPh arm [2]. Hence, we decided to functionalize the tacn ring with an aryloxy group, due to the more robust character of the M-O bond. The synthesis of $[\text{OH}(3,5\text{-}^t\text{Bu}_2\text{Ph})\text{-tacn}^{(\text{iPr}_2)}]$ has been achieved. As admitted, this ligand gave rise to well characterized $[\text{MCl}_2\{\text{O}(3,5\text{-}^t\text{Bu}_2\text{Ph})\text{-tacn}^{(\text{iPr}_2)}\}]$ ($\text{M} = \text{Ti}, \text{Y}, \text{Sm}$) complexes. These compounds could be derivatized to give alkyl complexes that are being checked in the polymerization of olefins.

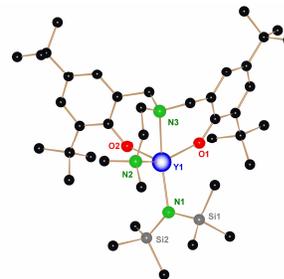


Molecular structure of $[\text{YCl}\{\text{O}(^t\text{Bu}_2\text{Ph})\}\text{-tacn}^{(\text{iPr}_2)}]$

Metal complexes, $[\text{TiCl}(\text{}^t\text{Bu}_2\text{O}_2\text{NN}')(\text{py})]$ and $[\text{YCl}(\text{}^t\text{Bu}_2\text{O}_2\text{NN}')(\text{DME})]$, supported by bis(phenolate)diamine ligands $\text{}^t\text{Bu}_2\text{O}_2\text{NN}'$ ($[\text{Me}_2\text{N}(\text{CH}_2)_2\text{N}\{\text{CH}_2\text{-}(2\text{-OC}_6\text{H}_2\text{-}^t\text{Bu}_2\text{-}3,5)_2\}]$), are also under investigation. Attempts to prepare a Ti(IV) cationic complex through reaction of $[\text{TiCl}(\text{}^t\text{Bu}_2\text{O}_2\text{NN}')(\text{py})]$ with $[\text{FeCp}_2]\text{PF}_6$ led to the isolation of $[\text{TiFCl}(\text{}^t\text{Bu}_2\text{O}_2\text{NN}')]$, attesting for the high electrophilicity of the transient titanium cation that is able to abstract a fluoride from the counter-ion. The

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synthesis of the amide $[\text{Y}\{\text{N}(\text{SiMe}_3)_2\}(\text{}^t\text{Bu}_2\text{O}_2\text{NN}')]^+$ and the alkyls $[\text{YR}(\text{}^t\text{Bu}_2\text{O}_2\text{NN}')]$ ($\text{R} = \text{CH}_2\text{SiMe}_3$, $\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2$) by halide metathesis of $[\text{YCl}(\text{}^t\text{Bu}_2\text{O}_2\text{NN}')(\text{DME})]$ shows that this compound is susceptible to further derivatization. The reactivity of the alkyls towards unsaturated substrates is under investigation. In contrast with the above, formation of a polymeric compound, $[\text{SmCl}(\text{}^t\text{Bu}_2\text{O}_2\text{NN}')]\text{x}$, was obtained in the reaction of samarium trichloride with the potassium salt of the diamino-bis(phenolate). Metathesis of the chloride led to formation of compounds containing the anion $[\text{Sm}(\text{}^t\text{Bu}_2\text{O}_2\text{NN}')_2]$, showing that one amino-bis(phenolate) is not enough to satisfy the bonding requirements of samarium.



Molecular structure of $[\text{Y}\{\text{N}(\text{SiMe}_3)_2\}(\text{}^t\text{Bu}_2\text{O}_2\text{NN}')]$

Studies on Ln/An separation continued in order to understand if one particular ligand is a promising ligand to effect the separation. The bond distances of a U(III) complex, used as a model for An, and La or Nd complexes (with similar ionic radii to that of U(III)) have to be compared in iso-structural complexes. Until now it was not possible to grow crystals adequate to X-ray crystal determinations.

Published work

- M.A. Antunes, M. Dias, B. Monteiro, A. Domingos, I.C. Santos, N. Marques, Synthesis and Reactivity of Uranium(IV) Amide Complexes Supported by a Triamidotriazacyclonane Ligand, *Dalton Trans.* (2006) 3368-3374.
- S. Barroso, J. Cui, A.R. Dias, M.T. Duarte, H. Ferreira, R.T. Henriques, M.C. Oliveira, J.R. Ascenso, A.M. Martins, Titanium(III) Trisamidotriazacyclonane: Reactions with C60 and Radicals, *Inorg. Chem.* 45 (2006) 3532-3537.

Gas-Phase Ion Chemistry of Actinides and Lanthanides*J. Marçalo, A. Pires de Matos, J. P. Leal, M. Santos, J. K. Gibson¹, R. G. Haire¹*

Fundamental aspects of the chemistry and physics of atomic and molecular actinide ions and neutrals continued to be examined by Fourier transform ion cyclotron resonance mass spectrometry (FTICR/MS). Experiments with atomic and molecular lanthanide ions were also performed for comparative purposes. Parallel theoretical studies of selected actinide molecular ions were also carried out via collaborations to substantiate the interpretation of the experimental observations.

The reactions of bare and oxo-ligated actinide cations (Th⁺ through Cm⁺) with small alkanes and alkenes were systematically studied. The reactivity trend identified for the highly reactive early actinide ions, Th⁺ > Pa⁺ > U⁺ > Np⁺, indicated significant 5f-electron participation in organoactinide σ -type bond formation for Pa⁺. Among the studied AnO⁺ ions, PaO⁺ was distinctively reactive. Electronic structure calculations showed that its ground state is Pa(5f6d)O⁺ and all excited states up to 1.8 eV have a 5f-orbital occupancy ≥ 0.8 . The high reactivity and substantial 5f character of PaO⁺ are a sign of the participation of 5f electrons in hydrocarbon bond activation for oxo-ligated Pa⁺.

New AnPt⁺ species (An = Th through Cm) were synthesized and the chemistries of UIr⁺, UPt⁺ and UAu⁺ examined in the context of “autogenic isolobality” and the theoretical prediction of strong actinide-transition metal bonds. The reactivities of the UM(5d)⁺ ions were dominated by the U metal center, in accord with the concept of “autogenic isolobality”. One noteworthy result was the synthesis of IrUO⁺ which was predicted to exist as a stable species isoelectronic with NUO⁺ and uranyl, UO₂²⁺.

¹ Oak Ridge National Laboratory (Oak Ridge, Tennessee, USA).

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 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, phenols and ionic liquids were studied.

During 2006, in addition to the determination of new enthalpies of formation for alkaline-earth and lanthanide compounds, the gas-phase acidity of substituted phenols was determined by using FTICR mass spectrometry. In a collaboration study with FCUL and ITQB, again using the FTICR/MS facility, the behavior of ionic liquids in the gas phase was studied showing that neutral ion-pairs are the only gas-phase molecules present. This opens the possibility to fractionally distill ionic liquids, thus allowing their purification.

A critically assessed compilation of existing enthalpies of formation for hydrocarbons was published and those values were used to parameterize an extended Laidler method of additive contributions. The newly parameterized method allows estimating 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. The extension of this model to CHON compounds is in progress. New routes for fluoroapatite synthesis were explored and their thermal and structural properties studied.

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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; however the number of active sites is very low (specific area < 1 m²/g). The main objective of this project is (i) to study binary copper/ or nickel/f-block element as catalysts or catalytic precursors and (ii) to develop new methods for the preparation of nanostructured materials that are currently the focus of considerable interest. Pursuing previous work, we have applied the urea-nitrate combustion method to the synthesis of BaO-La₂O₃ and MO-CeO₂ (M = Ba, Ca) nanoparticles, promising candidate catalytic systems for CO₂ valorization as C1 feedstock, namely through the selective oxidation of methane (OCM reaction). Preliminary results indicate that (i) the number of active sites is clearly superior to that measured on samples obtained by conventional methods, (ii) the f-block element plays a role in their acid-base properties and (iii) under industrial conditions (GHSV=42000 mLCH₄/g.h), the selectivity to C2 (C₂H₄+C₂H₆) on BaO-La₂O₃ is very high (> 95 %).

¹ ITN/Chemistry Sector-Solid State Group.

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. Pires de Matos*

Alkaline and alkaline-earth metal alkoxides are good models for rare-earth alkoxides and easier to synthesize. Some of the rare-earth alkoxides (Sc, Y, Ln) 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 phenoxides were synthesized. The used phenoxides possess different substituents and different substitution positions. The intention of this strategy is to understand the substituents contribution for the energetics/structure of the compounds. The measurement of the enthalpies of formation of the phenoxides was made by reaction-solution calorimetry and the structural characterization by powder X-ray and EXAFS.

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 glasses, mixtures of these glasses with sodium tetraborate glasses and tetraborate glasses have been used as hosts for uranium, thorium, cerium, terbium, holmium, and thulium oxides. Some preliminary conclusions were drawn for uranium and terbium: The intensity ratio MO^+/M^+ varies with the bond dissociation energy of the neutral oxide or the ion, the ratio MO^+/M^+ increases with the % of metal oxide added to the base glass and the borosilicate glasses in general shows a more strong M-O bond than the borates or sodocalcium silicate glass.

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 involves provenance studies of Portuguese glass from the 15th to the 20th century and the other concerns the development of new glasses for art applications. The historical glasses have started to be analysed by XRF spectrometry and by ICP/MS and the results obtained in an archaeological excavation in Coima were already reported in an international glass conference. Using some elements a series of new luminescent glasses with rare earths have been prepared, mainly using lanthanide oxides. Quenching of luminescence by d transition elements is being studied.

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.

Despite the fact that membranes naturally exhibit antimicrobial properties, the amoxicillin drug loaded membranes show an insignificant level of haemolysis 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. In these conditions, a maximum loading and release of amoxicillin was achieved.

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