COST Action CM1006

European f-Element Chemistry

EUFEN 1

April 2\textsuperscript{nd} to 4\textsuperscript{th} 2012

Universitat Rovira i Virgili
Tarragona
Spain
COST Action CM1006

European f-Element Chemistry

Date: April 2\textsuperscript{nd} to 4\textsuperscript{th} 2012

Meeting Place: Hotel Sol Costa Daurada
Tarragona
Spain

Local Organisers: Professor Francesc Díaz
Professor Magdalena Aguiló
Dr. Isabel Parreu
Dr. Maria Cinta Pujol

Timetable:

Monday 2\textsuperscript{nd} April 08.45 Start of Meeting
19.30 Buffet Dinner and Poster Session

Tuesday 3\textsuperscript{rd} April 09.00 All Day Talks
19.30 Gala Dinner

Wednesday 4\textsuperscript{th} April 09.00 Talks
12.00 Close of Meeting
TRAVEL TO TARRAGONA

Tarragona is a town about 80 kilometres south of Barcelona. It can be reached by a direct coach from Barcelona Airport - making it a convenient transfer journey.

This page covers the various options for transferring from Barcelona Airport to the centre of Tarragona. Options include train, coach, bus, car and taxi.

Guide to Transfer from Barcelona Airport to Tarragona

There are no direct trains from Barcelona Airport to Tarragona. Therefore, it is necessary to take a train into the centre of Barcelona to head out towards the south of Catalunya.

Take the Barcelona Airport Train -

The C2 to Estacio Sants (Barcelona Sants). If you are arriving into Terminal 1 (T1) you will not be able to walk straight to the train station, as it is 4km away. You will need to take a shuttle bus from outside the terminal -

At Estacio Sants you will need to change. There are an abundance of trains that run from Estacio Sants to Tarragona - approximately four every hour. The trains vary in journey time - some stopping at many stations and some direct.

To find out the time of this train it is necessary to go to the Renfe website -

The train that you will be catching does not have one particular name, as various trains travel through Tarragona - including the Catalunya Expres, the Regional expres, the Mare Nostrum, Alaris, Talgo and Euromed. The journey lasts between approximately 1 - 1.5 hours.

Transfer to Tarragona from Barcelona Airport by Train

There are no direct trains from Barcelona Airport to Tarragona. Therefore, it is necessary to take a train into the centre of Barcelona to head out towards the south of Catalunya.

Take the Barcelona Airport Train -

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Barcelona Airport Train Station
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To find out the time of this train it is necessary to go to the Renfe website - http://horarios.renfe.com/HIRRenfeWeb/buscar.do?O=BARCE&D=TARRA&ID=i&SF=3

The train that you will be catching does not have one particular name, as various trains travel through Tarragona - including the Catalunya Expres, the Regional expres, the Mare Nostrum, Alaris, Talgo and Euromed. The journey lasts between approximately 1 - 1.5 hours.

Transfer to Tarragona from Barcelona Airport by Coach

There is a coach that goes from Barcelona Airport to Tarragona. The Alsa Rápido Aeroport. There is a bus that leaves from outside T2 and then continues on to T1. It leaves four times a day and the journey lasts for 1 hour 15 minutes from T2 and 1 hour from T1. Check the Alsa Website for exact times and ticket prices - http://www.alsa.es/portal/site/Alsa

It is possible to reserve a ticket prior to your arrival at the airport.

Alsa Ticket Line
Tel: +34 91 327 0540

Transfer to Tarragona from Barcelona Airport by Bus

There is a direct coach from Barcelona Airport to Tarragona (see above). There is no normal TMB bus that runs from Barcelona to Tarragona.

You can first take the Aerobus Barcelona Airport Express Bus which has a stop at Plaça Espanya from both T1 and T2 - http://www.barcelona-tourist-guide.com/en/airport/transport/barcelona-airport-aerobus.html

From Plaça Espanya you can take the green line of the Metro two stops to Estacio Sants. From Estacio Sants you can take the train to Tarragona (see above for more details).

Conference Admin:

Plenaries: 50 minutes including questions.
Talks: 20 minutes including questions.
Posters: A0 portrait maximum size.
Monday 2\textsuperscript{nd} April

0845-0900 Opening

0900-1030 \textbf{Session 1. Chair - Karsten Meyer}

0900-0950 Plenary Lecture
Bill Evans, Irvine University, California
“Recent Results in the Reductive Chemistry of Rare Earth Metal Complexes”

0950-1010 Steve Liddle, University of Nottingham, UK
“Recent Results in the Construction of f-Block-Ligand Multiple Bond Linkages”

1010-1030 Ludovic Castro, Université de Toulouse - CNRS, France
“A theoretical approach of the Redox Chemistry of CO\textsubscript{2} with Lanthanide and Actinide Complexes”

1030-1100 BREAK

1100-1240 \textbf{Session 2. Chair - Anne-Sophie Chauvin}

1100-1120 Robert Baker, University of Dublin, Ireland
“Uranium (IV) Luminescence: New Tricks for an Old Dog”

1120-1140 Alistair Frey, University of Sussex, UK
“Small Molecule Activation at Low Valent Uranium Centres”

1140-1200 Richard Layfield, University of Manchester, UK
“Organometallic Dysprosium Single-Molecule Magnets”

1200-1220 Koen Binnemans, University of Leuven, Belgium
“Recycling of Rare Earths: Challenges and Opportunities”

1220-1240 Keith Izod, Newcastle University, UK
“Phosphine-Borane-Stabilised Carbanions as Ligands for Lanthanide (II) Ions”

1240-1400 BREAK

1400-1600 \textbf{Session 3. Chair - Fanny Bonnet}

1400-1420 Louise Natrajan, University of Manchester, UK
“Emissive Uranyl(VI) Oligomers Assembled by Uranyl-Oxo-Uranium Interactions”

1420-1440 Ivan Lukeš, Universita Karlova, Czech Republic
“Lanthanide Complexes with DOTA Analogues bearing Phosphorus pendant Arm”

1440-1500 Joris van Slageren, University of Stuttgart, Germany
“Electronic Structure of Lanthanide Double Deckers”

1500-1520 Jun Li, Tsinghua University, Beijing, China
“Exploring Excited States of Actinide Compounds”

1520-1540 Moris Eisen, Technion-Israel Institute of Technology, Israel
“New Reactivities Observed for Organoactinide Complexes”

1540-1600 Uwe Ruschewitz, University of Köln, Germany
“Lanthanide Coordination Polymers with Tetrafluoroterephthalate as Bridging Ligand”

1600-1640 BREAK
1640-1840  **Session 4. Chair - Francesc Diaz**

1640-1700  Abdou Boucekkine, University of Rennes 1, France  
“T Relativistic DFT Studies of Exchange Couplings in Bimetallic Uranium Complexes and of Electron Affinities of Uranium (IV) Complexes”

1700-1720  Ulrich Kortz, Jacobs University, Bremen, Germany  
“The Role of Lanthanides in Polyoxometalate Chemistry”

1720-1740  Andrew Kerridge, University College London, UK  
“Towards a Multiconfigurations Model of Actinide Coordination by Macrocyclic and Multidentate Ligands”

1740-1800  Jun Okuda, RWTH Aachen University, Germany  
“New Polydentate Ligands for Molecular Lanthanide Hydrides”

1800-1820  Antonella Dalla Cort, Universita La Sapienza, Roma, Italy  
“Uranyl-salophen Complexes: Versatile Building Blocks in Supramolecular Chemistry”

1820-1840  Carlos Platas-Iglesias, Universidade da Coruña, Spain  
“Polyamino Polypyrinecarboxylate Gd(III) Complexes as Potential Contrast Agents for Magnetic Resonance Imaging”

1840-1930  BREAK

1930-2200  **BUFFET DINNER AND POSTER SESSION**
Tuesday 3rd April

0900-1030  
Session 5. Chair – Keith Izod
0900-0950  
Plenary Lecture
Trevor Hayton, Santé Barbara University, California
“Synthesis of U=E Multiple Bonds via Oxidative Atom Transfer to U[N(SiMe3)2]3”
0950-1010  
Evgeny Kirillov, CNRS – Université de Rennes 1, France
“Rate Earth Complexes of New Multidentate Tethered Phenoxy-Amidinate Ligands: Synthesis, Structure and Applications in Rop of Lactide”
1010-1030  
Christoph Schädle, University of Tübingen, Germany
“Novel Hydride Transfer Reagents in Organolanthanide Chemistry”

1030-1100   
BREAK

1100-1240  
Session 6. Chair - Koen Binnemans
1100-1120  
Stéphane Petoud, Centre de Biophysique Moléculaire, Orléans, France
“Polymetallic Near-infrared Emitting Lanthanide Compounds: Dendrimer Complexes and Metal-organic Frameworks for Biological Imaging”
1120-1140  
Philippe Zinck, Université Lille Nord, France
“Coordinative Chain Transfer Polymerization: Recent Advances and a new Paradigm using rare Earth Catalysts”
1140-1200  
Karsten Meyer, University Erlangen-Nurnberg, Germany
“Activation and Functionalization of CO2 and Related Heteroallenes at Reactive Uranium Complexes”
1200-1220  
Olivier Maury, Laboratoire de chimie Lyon, France
“Two-photon Sensitized Lanthanides Luminescence: Bio-imaging applications from the Green to the Infra-red”
1220-1240  
Florian Jaroschik, Université de Reims, France
“Reduction of Cp2MCl2 (M = Ti, Zr) by Lanthanides: towards new Applications in Organic Synthesis”

1240-1400   
BREAK

1400-1600  
Session 7. Chair - Louise Natrajan
1400-1420  
Philip Mountford, University of Oxford, UK
“New Rare Earth and Alkaline Earth Metal-boron and Metal-metal Bonds”
1420-1440  
Tonya Vitova, Karlsruhe Institute of Technology, Germany
1440-1500  
Ana Maria Martinez, SINTEF , Trondheim, Norway
“Electrodeposition of Rare Earth Metals and Alloys from Molten Salts. An Overview”
1500-1520  
Thibault Cantat, CEA Saclay, France
“Uranium Complexes Featuring U=C Double Bonds”
1520-1540  
Gyula Tircsó, University of Debrecen, Hungary
“Lanthanide(III) Complexes of some Natural Siderophores: Thermodynamic, Kinetic and Relaxometric Study”
1540-1600  
Josef Hamacek, University of Geneva, Switzerland
“New Discrete 3D Complexes with Lanthanides. Design of Supramolecular Nanocapsules”

1600-1640   
BREAK
1640-1840  **Session 8. Chair - Michael Patzschke**

1640-1700  Marinella Mazzanti, CEA-Grenoble, France  
**“Structure, Magnetic Properties and Redox Reactivity of Schiff Base Complexes of 4f and 5f Elements”**

1700-1720  Julien Andres, EPFL-Lausanne, France  
**“Designing Water Soluble Lanthanide Complexes with Double Sensitization Ability”**

1720-1740  Maria Cinta Pujol, Universitat Rovira i Virgili, Tarragona, Spain  
**“Lu$_2$O$_3$ Sesquioxide Nanostructures for Photonics Applications”**

1740-1800  Ana F. Lucena, Instituto Tecnológico e Nuclear, Sacavém, Portugal  
**“Actinide Polysulfides in the Gas Phase”**

1800-1820  Iker Del Rosal, Université de Toulouse, France  
**“Supported Lanthanide Complex on Silica Surface: Grafting Mode and Reactivity”**

1820-1840  Maria Milanova, University of Sofia, Bulgaria  
**“Rare Earths Chemistry: Scientific, Technological and Production Activity at the Department of Inorganic Chemistry, Sofia University”**

1930-2200  **GALA DINNER**
### Wednesday 4th April

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<td>Plenary Lecture</td>
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<td>Karl Gschneidner Jr, Ames Laboratory, Iowa State University</td>
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<td>“Materials/Inorganic Chemistry of the Rare Earth Elements”</td>
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<td>0900-0950</td>
<td>Daniel Imbert, CEA-Grenoble, France</td>
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<td>“Coordination and Photophysical Properties Homo- and Hetero-metallic Complexes, Multimodal Imaging Agents”</td>
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<td>1010-1030</td>
<td>Emad Borai, Atomic Energy Authority, Egypt</td>
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<td>“Group Separation of Heavy Metals followed by Subsequent and Individual Separation of Lanthanides by Chelation Chromatography”</td>
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<tr>
<td>1100-1200</td>
<td>Polly Arnold, University of Edinburgh, UK</td>
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<td>“Bond Activation Chemistry with Rare-earth Metal N-heterocyclic Carbene Complexes”</td>
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<td>1120-1140</td>
<td>Pekka Pyykkö, University of Helsinki, Finland</td>
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<td>“Rare-earth Monocarbonyls MCO: Comprehensive Infrared Observations and a Transparent Theoretical Interpretation for M = Sc; Y; La-Lu”</td>
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<td>1140-1200</td>
<td>Jaume Cugat, Universitat Rovira i Virgili, Tarragona, Spain</td>
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<td>“Rib Waveguides Fabricated by fs-laser Ablation on (Yb, Nb): RbTiOPO₄/ RbTiOPO₄ Epilayers”</td>
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Plenary Lectures
Recent Results in the Reductive Chemistry of Rare Earth Metal Complexes

William J. Evans*

Department of Chemistry
University of California, Irvine California 92697-2025
*e-mail: wevans@uci.edu

The reductive chemistry of the rare earth metals, i.e. Sc, Y, and the lanthanides, was at one point limited to the chemistry of Eu$^{2+}$, Yb$^{2+}$, Sm$^{2+}$, and the zero valent metals. The field has expanded greatly since that time: new +2 oxidation state species have been identified and methods of doing reduction with ligands in complexes of redox inactive metal ions have been discovered. This talk will describe recent advances in this area as well as implications for the future of the field.
Synthesis of U=E Multiple Bonds via Oxidative Atom Transfer to U[N(SiMe$_3$)$_2$]$_3$

Jessie L. Brown, Skye Fortier, Guang Wu, and Trevor W. Hayton*

Department of Chemistry and Biochemistry, University of California, Santa Barbara CA USA 93106

*e-mail: hayton@chem.ucsb.edu

We are exploring the atom transfer chemistry of the well known U(III) amide complex U(NR$_2$)$_3$ (R = SiMe$_3$, 1) with a variety of reagents, including azides, amine-N-oxides, TEMPO, and elemental chalcogens, in an attempt to form complexes possessing U=E multiple bonds. For example, reaction of 1 with TEMPO results in clean formation of a terminal U(V) oxo, U(NR$_2$)$_3$(O) (2), in good yield.$^{1,2}$ Similarly, reaction of TEMPO with U(NR$_2$)$_3$(CH$_2$=PPh$_3$) (3) results in formation of another terminal oxo, [Ph$_3$PCH$_3$][U(O)(CH$_2$SiMe$_2$NSiMe$_3$)(NR$_2$)$_2$] (4), also in good yield.$^3$ These are rare examples of the use of TEMPO as an O-atom transfer reagent. In contrast, reaction of 1 with a traditional O-atom source, such as Me$_3$NO, results solely in formation of the U(IV) bridging oxo, [U(NR$_2$)$_3$]$_2$(μ-O) (5). These studies suggest a role for the development of new atom transfer reagents in the synthesis of novel U=E bonds. The reactivity of complexes 2 and 3 with other atom transfer reagents, such as chalcogenide sources, will also be described.


The rare earth chemistry is dominated by the trivalent state and fairly large atomic sizes (metallic radii: 1.879 [La] to 1.735 [Lu] to 1.641 [Sc]; ionic radii: 1.061 [La] to 0.848 [Lu] to 0.732 [Sc]). However, a number of the lanthanides have other valence states 4+ (Ce, Pr, Tb) and 2+ (Sm, Eu, Yb). In the trivalent state the binding energies are nearly the same for neighboring lanthanides, but the 4f contribution to the bonding in many cases is sufficient to change the energetics, which can account for differences in the variation of crystal structures, free energies of formation, melting points, etc. along the lanthanide series. The 4f electrons that hybridize with the bonding electrons are not the localized 4f electrons which account for the observed magnetic and optical properties, but are from the low lying electronic levels above the Fermi level which have a band-like character. The dual localized, band-like model was proposed about 40 years ago from a systematic global analysis of the physical properties of the rare earth metals [1] and confirmed from first principal calculations about 20 years later [2]. When carrying out such a systematic global analysis it is critically important to include Y and Sc; one cannot work alone with the lanthanide – some interesting correlations and science may be lost. In some cases one also needs to include some of the non-rare earth elements (Groups 1 to 5) in such analyses.

Examination of the thermodynamic properties of rare earth compounds, e.g. R₂O₃ phases, the values of Eu³⁺ and Yb³⁺ are anomalous relative to the other R³⁺ elements. This is due to the fact that all such properties are calculated from the standard state of the rare earth metal at 1 atmosphere pressure and 298 K, and Eu and Yb are both divalent in the metallic state while the other rare earth metals are trivalent. Thus the energy required to promote Eu²⁺ and Yb²⁺ to the trivalent state must be taken into account, and this positive contribution (88 and 46 kJ/g.at., respectively) reduces the negative free energy of formation of these two trivalent elements by this amount respectively [3].

Session Talks
Recent Results in the Construction of f-Block-Ligand Multiple Bond Linkages

Oliver J. Cooper, David M. King, David P. Mills, Stephen T. Liddle*

School of Chemistry, University of Nottingham, University Park,
Nottingham, NG7 2RD, UK

*e-mail: stephen.liddle@nottingham.ac.uk

Compared to the extensive literature on transition metal-ligand multiple bond linkages that of analogous f-block complexes can, with certain notable exceptions, be considered to be far less developed. There is therefore significant interest in f-block-ligand multiple bond linkages in terms of their nature and reactivity.

We will present our recent work on f-block-carbenes which exhibit formal covalent M=C double bonds.1-4 In particular, for uranium we will show that U=C double bonds covering all commonly accessible oxidation states of uranium (IV-VI) are accessible after nearly thirty years of being limited to U(IV)=C.

If time allows we will describe our recent work on other f-block-ligand multiple bond linkages.

The transformation of CO$_2$ and especially its reduction is an important environmental issue. In the last ten years, molecular systems involving either Samarium(II) or Uranium(III) centers have been reported to be efficient to reduce CO$_2$. However, depending on the nature of the metal and of the ligands, formation of either carbonate or oxalate complexes have been experimentally observed. In this presentation, after briefly discussing the relative influence of the f electrons in the reactivity of organolanthanide and actinide complexes as well as a methodology to compute oxidation of f-element complexes, I will discuss the reaction mechanism for CO$_2$, COS and CS$_2$ reduction by Cp*2Sm, (Cp*)(COT)U and N-anchored aryloxide U(III) complexes. It will be demonstrated that this difference of reactivity is mainly explained by steric effects.
Uranium(IV) Luminescence: New Tricks for an Old Dog

Robert J. Baker,* Emtithal Hashem and James A. Platts

School of Chemistry, University of Dublin, Trinity College, Dublin 2, Ireland

bakerrj@tcd.ie

The photophysics of the uranyl (UO$_2^{2+}$) moiety has been well studied,$^1$ but the lower oxidation states have not been examined in much detail. There is only one report of fluorescence from a U(IV) compound.$^2$ We will present studies on the photophysics of selected uranium(IV) compounds, [Li(THF)$_4$][UCl$_5$(THF)], [Et$_4$N]$_2$[UCl$_6$] and [Et$_4$N]$_4$[U(NCS)$_8$],$^3$ that display emissions that originate from excitation into the f-orbital manifold. A comprehensive computational study on some of these compounds will also be presented, and these show substantial overlap between the Cl 3p orbitals and U 5f and 6d orbitals.

Small Molecule Activation at Low Valent Uranium Centres

Alistair S. P. Frey, a F. Geoffrey N. Cloke*, a Laurent Maron, b
Thomas Davin, b Martin P. Coles, a S. Mark Roe a

a Division of Chemistry, School of Life Sciences, University of Sussex,
Brighton BN1 9QJ, UK
b LPCNO, INSA Toulouse, 31077 Toulouse, France

*e-mail: f.g.cloke@sussex.ac.uk

Uranium(III) complexes featuring bulky silylated cyclooctatetraenyl ligands (e.g. A) have been found to engage in reductive cyclooligomerisation of CO to form oxocarbon dianions.1,2,3 Recent work has focused on co-reactions of NO and H2 with CO, resulting in the formation of U(IV) cyanate4 (B) and methoxide5 (C) complexes. Recent developments will be presented, including experimental and theoretical studies to elucidate the mechanism of these remarkable transformations.

Organometallic Dysprosium Single-Molecule Magnets

Richard A. Layfield,*a Liviu F. Chibotaru,b David Collison,a Jun Okuda,c Charlene A. Smith,a Scott A. Sulway,a Floriana Tuna,a Ajay Venugopalc and Richard E. P. Winpennya

aSchool of Chemistry, The University of Manchester, Manchester M13 9PL, U.K.
bDivision of Quantum and Physical Chemistry, Katholieke Universiteit Leuven, Belgium
cInstitute of Inorganic Chemistry, RWTH Aachen, Landoltweg 1, D-52056 Aachen, Germany

*Richard.Layfield@manchester.ac.uk

Single-molecule magnets (SMMs) are molecules that have a magnetic memory. The ability of zero-dimensional, molecular objects being able to retain magnetization means that they can, in principle, be used for advanced applications in high-density information storage and as molecular spintronic materials.1

Certain properties must be taken into account in the design of SMMs. The molecule should have: a high magnetic moment; significant magnetic anisotropy; and a bistable ground state. If these conditions are met, a molecule might be an SMM. From this point, whether or not a molecule is an SMM, and thence an efficient SMM, requires a combination of rational design and a hint of serendipity.

Undoubtedly, some of the most eye-catching SMMs are lanthanide (Ln) compounds.2 In particular, the electronic structure of dysprosium(III) has enabled the development of SMMs that function much more efficiently than those based on d-transition metals.3

Now that the field is maturing, the balance of design versus providence is gradually tipping in favour of targeted outcomes: enhancing anisotropy via crystal field symmetry and strength, and via magnetic exchange, is crucial. Thus, organometallic chemistry offers advantages over the methods of “classical” coordination chemistry, which have to date delivered Ln-SMMs based largely on oxygen-donor ligands.

In 2010, we reported the first organometallic SMM (1), and have subsequently developed other organo-dysprosium SMMs based on “non-classical” ligands (2).4 Our studies have recently been extended to include the first thiolate-bridged (3)5 and hydride-bridged (4)6 SMMs, whose magnetic memory properties will be presented.

In support of experimental studies, ab initio calculations have enabled accurate modelling of the magnetic exchange in our Dy-SMMs. These calculations have identified the orientation of the Dy anisotropy axes, which should in principle enable the rational development of new Ln-SMMs with enhanced magnetic memory effects.

The rare-earth elements (REEs) are becoming more and more important, because of their essential role in permanent magnets, lamp phosphors, catalysts and rechargeable batteries. The increasing popularity of hybrid and electric cars, wind turbines and compact fluorescent lamps is causing an unprecedented increase in the demand and price of REEs. In its landmark report Critical Raw Materials for the European Union (2010), the European Commission considers the REEs as the most critical elements, with the highest supply risk. With China presently producing more than 97% of the global production of the REEs, Europe is heavily dependent on China, even though it possesses less than 40% of the proven reserves. China is not only mining REEs, but is also specialised in the extraction of REEs from ores, in the separation of concentrates of REEs in the individual elements, and in the production of REE permanent magnets and lamp phosphors from purified REEs. Because of large domestic demands, China tightened its REE export quota from 50.145 tonnes in 2009 to only 31.130 tonnes in 2012. This causes serious problems for consumers of REEs outside China, and also for the development of a more sustainable, low-carbon economy. Mining companies are now actively seeking for new exploitable rare earths deposits and old mines will be reopened. For instance, the Mountain Pass Mine in California will restart production in 2012. Because there are hardly any exploitable natural resources of REEs in Europe, opening of new mines is unlikely in the near future and Europe has to rely on recycling of REEs from pre-consumer scrap and (often complex, multi-material) End-of-Life products (“urban mining”). However, as recently pointed out in the influential UNEP report Recycling Rates of Metals (2011), less than 1% of the REEs are currently being recycled, mainly due to inefficient collection, technological problems and (until now) lack of incentives. Furthermore, used permanent magnets and other REE-containing waste are currently shipped back to China, resulting in a significant loss of valuable resources. A drastic improvement in End-of-Life recycling rates for REEs in Europe is, therefore, an absolute necessity, in line with the goals of the EU’s Roadmap to a Resource Efficient Europe (2011). This can only be realised by developing new efficient recycling routes. This talk will give an overview of the problems and possible solutions associated with the recycling of the rare earths two main applications of REEs: permanent magnets and lamp phosphors. These two applications represent more than 70% of the rare-earth market by value. Special emphasis will be paid to the development of sustainable closed materials loops for the rare earths.¹

Phosphine-Borane-Stabilised Carbanions as Ligands for Lanthanide(II) Ions

Keith Izod, * William Clegg, Ross W. Harrington

School of Chemistry, Newcastle University, Newcastle upon Tyne NE1 7RU, UK

*e-mail: keith.izod@ncl.ac.uk

Low oxidation state lanthanide complexes mediate a remarkable and diverse array of organic reactions and small molecule transformations. Within this field some of the most impressive chemistry is mediated by complexes with sterically demanding, substituted cyclopentadienyl ligands such as Cp* and 1,3-(Me3Si)2C5H3. Given the unusual chemistry mediated by these species, it is perhaps surprising that the chemistry of the related lanthanide(II) dialkyls, R2Ln, remains largely undeveloped and that few such compounds have been reported. In this regard, the first samarium(II) dialkyl, [(Me3Si)2(Me2MeOSi)C]2Sm(THF) (1), was reported only in 1997 and its reactivity has barely been explored.1 Efforts to synthesise analogous Tm(II) dialkyls have led to unexpected ligand degradation and coupling reactions.2

As part of an ongoing project, we are investigating the chemistry of phosphine-borane-stabilised carbanions and, in an effort to expand the range of stable lanthanide(II) dialkyls and to probe their reactivities, recently reported the first lanthanide(II) derivatives of these ligands, [(Me3Si)2{Me2P(BH3)}C]2Sm(THF)ₙ (n = 3, 2a; n = 1, 2b), both of which crystallise as THF adducts.3 Somewhat surprisingly, in contrast to 2, the homoleptic, solvent-free ytterbium(II) analogue [(Me3Si)2{Me2P(BH3)}C]2Yb (3) reacts rapidly with THF. The reactivities of 2 and 3 are currently being investigated.

Ascertaining the chemical forms of actinide ions and developing a detailed understanding of their chemical behaviour lies at the heart of the successful implementation of new waste management and reprocessing strategies in the nuclear fuel cycle. Current methods of monitoring actinide migration are based on radiometric counting techniques, are relatively insensitive and provide no information regarding speciation or oxidation state. On the other hand, time resolved luminescence spectroscopy is an excellent tool with which to study actinide forms. Here, will present a family of emissive uranyl(VI) complexes and demonstrate that the form of the emission spectra are sensitive to the nature of the ligand bound in the equatorial plane and the complex nuclearity (extent of aggregation). Furthermore, uranyl(VI) oligomers assembled by uranyl-oxo-uranium interactions ('cation-cation' interactions) can be identified in solution and the solid state by emission spectroscopy, potentially giving a sensitive method of assessing the form and speciation of uranyl complexes in solution.\textsuperscript{1} Our results in this area will be presented with a discussion of their photophysical properties.

Spectral identification of Uranyl(VI) oligomers

Lanthanide Complexes with DOTA Analogues Bearing Phosphorus Pendant Arm(s)

Ivan Lukeš

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Series of DOTA analogues having phosphorus-based coordinating pendant arm(s) was studied due to their possible medicinal use, especially as ligands for MRI contrast agents and/or for the use in radiomedicine. From point of view of MRI applications, the presence of phosphorus-based group in the molecule generally brings several advantages: higher abundance of twisted-square antiprismatic species, which have generally fast water-exchange rate due to flexible coordination sphere; network of strong hydrogen bonds, resulting in high second/outer-sphere relaxivity contribution; and easy introduction of bifunctionality through phosphinate pendant group. Several bifunctional derivatives were prepared and conjugated to selected macromolecular carriers in order to slowing down molecular tumbling of the Gd(III) complexes, what resulted in significant increase in longitudinal relaxivity. For this reason, short and rigid spacers between phosphorus atom and reactive side-groups are needed; as the bifunctional groups, side-arm amino, carboxylate or alkyne groups can be easily introduced. Kinetic stability of the lanthanide(III) complexes is also usually sufficient for possible medicinal utilizations.

Figure 1: Schematic structure of the ligands discussed.
Electronic Structure of Lanthanide Double Deckers

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We present a comprehensive study of the electronic properties of the lanthanide double deckers [LnPc2]0/- (Pc = phthalocyanine) in all relevant energy ranges. We have studied the properties of the ground state by means of (pulse) electron paramagnetic resonance and have obtained information on the hyperfine coupling, spin coupling, and the spin dynamics. We have studied the crystal field splittings by means of far-infrared and inelastic neutron scattering spectroscopy, allowing the accurate determination of the crystal field splitting parameters. Furthermore, we have studied the electronic structure and magnetization dynamics by means of magnetic circular dichroism spectroscopy. Finally, we will discuss the influence of substitution of the phthalocyanine ring on the magnetic and electronic properties of the complexes.
Exploring Excited States of Actinide Compounds

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Actinide chemistry is an essential part of nuclear and radiochemistry. Theoretical investigations are required to provide detailed and fundamental understanding of the ground-state and excited-state properties of actinide compounds. While computational modeling of excited states of actinide compounds is challenging due to complicated electron correlation and relativistic effects, progress has been made in the recent years in interpreting electronic spectra of actinide systems. In this talk we will present our computational investigation results on the structures, stabilities, excitation energies, and fluorescence spectroscopic properties of actinide complexes using relativistic quantum chemistry methods. We have investigated the optimal structures and excitation energies of UO$_2^{2+}$, NUO$^+$, UN$_2$, UF$_6$, (Ar)$_x$UO$_2$Cl$_2$, NpO$_2$Cl$_4^{2-}$ and hydrated uranyl-glycine-water complexes using relativistic wavefunction theory (WFT) and density functional theory (DFT).[1-4] The calculated excitation energies and simulated fluorescence spectra using a time-dependent theory of electronic spectroscopy are in good agreement with experiments. We will also present perspectives on applying spin-orbit coupled approach to large actinide compounds.

References:
New Reactivities Observed for Organoactinide Complexes

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Neutral and cationic organoactinide complexes have been extensively studied in the last decade as catalysts for several organic transformations. Polymerization of alkenes, oligomerization, intermolecular hydroamination, and hydrosilylation of terminal alkynes, and 1,1-insertion of isonitriles into terminal alkynes comprise some of these processes. However, due to the high oxophilicity of the actinide complexes, all the substrates containing oxygen atoms were excluded because of the expected low activity of these complexes due to the predictable oxygen-actinide interaction. In our attempts to discover new catalytic reactions for actinide-based complexes, we have found their surprising activity towards the polymerization of cyclic mono- and diesters. This discovery arouses the conceptual question about the activity of oxo-actinide complexes.1 To expand the scope of the actinides in catalysis, we have pursued the dimerization of aldehydes to esters.2 In order to show the generality of the process, and to be able to proposed a suitable mechanistic pathway, we have investigated various organoactinide complexes in addition to kinetic and thermodynamic studies. In addition, in this contribution we will also present the synthesis, characterization of oxide-bridged uranium complexes, and the catalytic reactivity for the metathesis reaction of silylalkynes, phenylsilane and the C-H activation of arenes.


The synthesis of metal-organic framework compounds (MOFs) is in the focus of many research groups world-wide. The interest in this class of materials is driven by their structural versatility as well as potential applications, e.g. adsorption of gases, catalysis, drug delivery. Apart from that, they can also show interesting magnetic and optical properties.\cite{Ferey2008}

In 2006 Chen et al. compared the luminescence properties of two Er\(^{3+}\) coordination polymers with perfluorinated and non-fluorinated terephthalates as linkers. No C-H quenching effects occurred for the coordination polymers with the perfluorinated linker, which resulted in superior emission properties.\cite{Chen2006}

After improving the synthesis of H\(_2\)tfBDC,\cite{Orthaber2010} we were able to synthesize numerous new single crystalline coordination polymers containing transition metals or lanthanides and tfBDC\(^{2-}\) as linker.\cite{Seidel2011, Seidel2012} The crystal structures, thermal, absorption and emission properties of coordination polymers of general composition \(\left[\text{Ln(tfBDC)(NO}_3\text{(DMF)}_2\right] \cdot \text{DMF with Ln} = 4f\) elements have been investigated.\cite{Seidel2012} In this contribution we would like to summarize these results and will present bimetallic compounds with general formula \(\left[\text{Ln}_{x}\text{Ln}’_{1-x}(\text{tfBDC})(\text{NO}_3\text{(DMF)}_2\right] \cdot \text{DMF.}

Combining different lanthanide cations in one bimetallic compound should lead to tunable and improved emission properties. To prove this assumption we have performed detailed luminescence measurements, which will also be presented.


Relativistic DFT Studies of Exchange Couplings in Bimetallic Uranium Complexes and of Electron Affinities of Uranium (IV) Complexes

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Exchange couplings between uranium atoms in binuclear complexes have been investigated using Relativistic DFT calculations within the ZORA framework, combined with the broken-symmetry (BS) approach, using the ADF2010 program. Several systems have been studied, covering different oxidation states (V, IV and III) of uranium, giving rise to the following cases: 5f¹-5f¹, 5f²-5f² and 5f³-5f³. For example, in the case of the para imido diuranium(V) complex [(C₅H₄)₃U₂(µ-1,4-N₂C₆H₄)], we found that contrarily to the B3LYP hybrid functional, the BP86 one fails to predict the actual antiferromagnetic behaviour of the complex. Spin polarization is exalted by the effective participation of the 5f metal orbitals in bonding whereas the imido ligand plays also a key role permitting electronic and magnetic communication between the two active 5f¹ electrons of U(V) ions. Results for U(III)-U(III) and U(IV)-U(IV) binuclear uranium complexes will also be presented.

The redox behaviour of several series of biscyclopentadienyl, triscyclopentadienyl and phospholyl uranium(IV) complexes has been also studied theoretically. The investigations bring to light the importance of spin-orbit coupling and solvent effect and the use of a large basis set in order to achieve a good agreement (correlation coefficient $r^2$ equal to 0.99) between computed electron affinities of these U(IV) complexes and their half-wave reduction potentials measured by electrochemistry.
Polyoxometalates (POMs) are discrete, anionic metal-oxides, usually formed by early-transition metals in high-oxidation states (e.g. Mo$^{6+}$, W$^{6+}$, V$^{5+}$) with an enormous structural and compositional variety, and with potential applications in diverse areas such as catalysis, magnetism, bio- and nanotechnology, medicine, and materials science.\textsuperscript{1} Lanthanide-containing POMs may exhibit interesting luminescence, magnetic, and Lewis acid catalytic properties.\textsuperscript{2} Our group has been studying the interaction of lanthanide ions with polyoxotungstates and -palladates. We have synthesized the very large, dimeric, 20 cerium(III)-containing 100-tungsto-10-germanate $\left[\text{Ce}_{20}\text{Ge}_{10}\text{W}_{100}\text{O}_{376}(\text{OH})_{4}(\text{H}_{2}\text{O})_{30}\right]^{56-}$ under conventional reaction conditions from the trilacunary POM precursor $\left[\alpha-\text{GeW}_{9}\text{O}_{34}\right]^{-10}$ and Ce$^{3+}$ ions.\textsuperscript{3} We also encapsulated different lanthanide ions in a polyoxopalladate(II) nanocube, leading to the series $\left[X^{II\text{Pd}^{II}12(\text{AsPh})_{8}\text{O}_{32}}\right]^{5-}$ (X = Y, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). The Gd$^{3+}$-derivative showed interesting magnetic properties.\textsuperscript{4} The unexpected open ring polyanion $\left[\text{Fe}_{16}\text{O}_{2}(\text{OH})_{23}(\text{H}_{2}\text{O})_{9}\text{P}_{8}\text{W}_{49}\text{O}_{189}\text{Ln}_{4}(\text{H}_{2}\text{O})_{20}\right]^{11-}$ (Ln = Eu$^{3+}$, Gd$^{3+}$) can be easily prepared by reaction of the cyclic $\left[\text{H}_{2}\text{P}_{8}\text{W}_{48}\text{O}_{184}\right]^{33-}$ polyanion with Fe$^{3+}$ and Ln$^{3+}$ ions in acidic aqueous medium and in the presence of hydrogen peroxide.\textsuperscript{5}

Towards a Multiconfigurational model of Actinide coordination by Macrocyclic and Multidentate Ligands

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Over the past decade there has been continued interest in the coordination of actinyl ions, \([\text{AnO}_2^{2+}]^{1/2+}\), by expanded porphyrins, in particular hexaphyrin(1.0.1.0.0.0) (isoamethyrin), as first shown by Sessler et al [1]. Expanded porphyrins show promise as actinide sensors and may have potential in An(III)/Ln(III) separation [2]. The multidentate bonding character of the ligand is also reminiscent of those used in An(III) extraction, such as BTP [3]. The macrocycle allows variation in both the number and nature of coordinating species, as well as significant conformational flexibility via the inclusion of bridging carbons between pyrrole units (see Figure 1), and hence has the potential to be tuned for selective binding. These characteristics mean that, in addition to their potential applications, these complexes are particularly suitable for studies of fundamental characteristics of f-element chemistry. This makes computational studies of expanded porphyrin complexes of actinyls relevant to both industry and academia.

The modelling of the open f-shell of the actinides presents a significant computational challenge, and multiconfigurational methods (such as the complete-active-space self-consistent-field, or CASSCF, approach) are often preferred, and sometimes required. However, CASSCF is computationally intensive, and is impractical for the systems discussed here. We are in the process of developing a RASSCF-type approach which will allow for the accurate simulation of these complexes with a substantial reduction in computational cost. Preliminary results of this approach will be presented, along with density functional theoretical (DFT) studies of U, Np and Pu expanded porphyrin complexes.

Figure 1. Structural variation in uranyl hexaphyrin, dependent on inclusion of bridging carbons

New Polydentate Ligands for Molecular Lanthanide Hydrides

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Solid state interstitial hydrides with the composition LnH_x (x < 3) such as LaNiH_5 attracts attention as hydrogen storage materials. Obviously, simple molecular hydrides of the composition LnH_n (n = 2, 3, 4) of rare earth metals are not isolable under standard conditions. When stabilized by suitable ancillary ligands they could give valuable insights into the molecular processes associated with hydrogen uptake and release. Coordinative saturation achieved by metallocene scaffolds [M(η^5-C_5R_5)_2] resulted in a rich chemistry of group 3 metals hydride complexes. The use of polydentate ligands such as Me_nTACD (n = 3, 2) or Me_6TREN now allowed the preparation and isolation of several new types of molecular hydrides of the lanthanides.

The absence of sterically bulky and electron donating cyclopentadienyl ligand results in a more ionic metal-hydrogen bonds that along with the large metal size causes aggregation to give polynuclear species. The introduction of cationic derivatives gave relatively discrete units and led to the observation of dihydrogen activation reaction that involves intramolecular C-H bond activation of the ligand’s peripheral substituents.

Salophens are one of the oldest and most popular class of ligands in coordination chemistry because of their versatility and easy synthetic availability. It is well known that salophen ligands are able to stabilize many different metals in various oxidation states. The role of the metal center in determining the characteristics of these complexes is fundamental and various. The majority of such metal-salophen complexes can be described as immobilized Lewis acids able to coordinate Lewis bases by accommodating them in the apical positions or in the equatorial ones, if present.

In the last years our research interest has been focused on the use of Uranyl-salophen complexes, 1, as anion receptors, supramolecular catalysts and building blocks for supramolecular assemblies. This contribution will highlight some of these aspects and some of our most recent results obtained with new Uranyl-complexes, 2, performing anion recognition in water.

Polyamino Polypyridinecarboxylate Gd(III) Complexes as Potential Contrast Agents for Magnetic Resonance Imaging

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Stable Gd\textsuperscript{III} complexes with polyaminocarboxylate ligands are commonly used as contrast agents (CAs) in Magnetic Resonance Imaging (MRI).\cite{1} CAs are paramagnetic molecules that enhance the image contrast by shortening the longitudinal and/or transversal relaxation times of protons in water molecules in the vicinity of the chelate. CAs must be stable enough, both from the thermodynamic and kinetic point of view, to avoid the \textit{in vivo} release of toxic free Gd\textsuperscript{III}. The issue of Gd\textsuperscript{III} toxicity is receiving much attention nowadays, as a the recently described disease, nephrogenic systemic fibrosis, has been identified in patients with severe renal failure. This might be associated with the use of Gd\textsuperscript{III} contrast agents based on DTPA-bisamide derivatives, which show a relatively fast dissociation kinetics.\cite{2} In this contribution a series of ligands designed for stable Gd\textsuperscript{III} complexation in aqueous solution will be presented. These octadentate ligands contain pyridylcarboxylate groups that ensure a high stability and solubility of their complexes in water. On the basis of structural considerations, we were able to control the water exchange rate of the inner sphere water molecule in the corresponding Gd\textsuperscript{III} complexes, an important parameter to be optimized in order to obtain efficient MRI contrast agents. A detailed study of the structure of the complexes in aqueous solution (NMR and DFT calculations) and in solid state (X-Ray diffraction studies) will be presented.


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Rare Earth Complexes of New Multidentate Tethered Phenoxy-Amidinate Ligands: Synthesis, Structure and Applications in ROP of Lactide

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Given the success of the “constrained geometry” Cp-amido complexes of early transition metals in polymerization catalysis, the implementation of new ligand assemblies incorporating tethered anionic moieties can be of both fundamental and practical value.

New multidentate tethered amidine-phenol pro-ligands {4,6-tBu2C6H2O-(2-C(N-R)=N-R}H2 ({LONR}H2, R = iPr, cyclohexyl (Cy), 2,6-iPr2C6H3 (Ar)) were synthesized and their coordination chemistry with rare earth metals (Y, Nd, Sm and Yb) has been investigated. 1 Three different approaches were explored to coordinate these (pro)ligands onto rare earths: salt metathesis, and amine and methane elimination reactions. Thus, chloro, amido and alkyl complexes of group 3 metals have been obtained and authenticated. Two alternative coordination modes of this dianionic ligand (I and II) and a protonated mono-anionic form (III) have been evidenced in complexes:

Amido complexes of phenoxy-amidinate ligands are active initiators/catalysts, when combined with iPrOH or PhCH2OH used as co-initiators/chain transfer agents, in the ROP of rac-lactide, giving atactic to heterotactic-enriched PLAs. Studies on the catalytic activity of these complexes will be detailed.

Organolanthanide hydride complexes play an important role in a variety of catalytic transformations, such as polymerization of isoprene or ethylene, olefin hydrogenation and hydrosilylation. Previously our group reported on the hydrogenolysis of ansa-lanthanidocene complex \( \text{rac-}[\{\text{Me}_2\text{Si}(2-\text{Me-C}_9\text{H}_5)_2\}Y\{\text{N(SiHMe}_2}\}_2]\) using diisobutylaluminum hydride (DIBAH). Although DIBAH is used in industrially applied catalyst mixtures, e.g., \( \text{Nd(OCOR)}_3/\text{Et}_3\text{Al}_2\text{Cl}_3/\text{DIBAH} \) (ratio: 1:1:8), the reaction pathway of the hydride transfer is still not well understood. In the current study we sounded out the reactivity of selected alkylaluminum hydrides such as \( \text{HAlMe}_2 \), \( \text{HAl(CH}_2\text{SiMe}_3)_2 \), and \( \text{H}_2\text{AlMes}^* \) (Mes* = 2,4,6 tris-\( t \)-butylbenzene) toward a series of lanthanide alkyl complexes. Direct hydride transfer as well as formation of distinct adduct complexes could be observed. The corresponding products were characterized by spectroscopic methods (IR, NMR) and X-ray structure analysis.

Polymetallic Near-infrared Emitting Lanthanide Compounds: Dendrimer Complexes and Metal-organic Frameworks for Biological Imaging

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Fluorescence and luminescence are detection techniques that possess important advantages for bioanalytical applications and biologic imaging: high sensitivity, versatility and low costs of instrumentation. A common characteristic of biologic analytes is their presence in small quantities among complex matrices such as blood, cells, tissue and organs. These matrices emit significant background fluorescence (autofluorescence), limiting detection sensitivity.

The luminescence of lanthanide cations has several complementary advantages over the fluorescence of organic fluorophores and semiconductor nanocrystals, such as sharp emission bands for spectral discrimination from background emission, long luminescence lifetimes for temporal discrimination and strong resistance to photobleaching. In addition, several lanthanide cations emit near-infrared (NIR) photons that can cross deeply into tissues and that result in improved detection sensitivity due to the absence of native NIR luminescence from tissues and cells. The main requirement to obtain lanthanide emission is to sensitize them with an appropriate chromophoric sensitizer.

An innovative concept for the sensitization of lanthanide cations is proposed herein; the current limitation of low quantum yields experienced by most mononuclear lanthanide complexes is compensated for by using a large number of lanthanide cations and by maximizing the absorption of each discrete molecule, thereby increasing the number of emitted photons per unit volume and the overall sensitivity of the detection. To apply this concept, we are developing several families of compounds that incorporate several lanthanide cations and that have large absorptivities. We will present in this paper concepts, synthesis, characterization and luminescence properties for two families of compounds: 1) nanoscale dendrimers complexes and 2) metal-organic frameworks. We will also describe several examples of applications of these compounds as NIR reporters for biologic imaging in living cells and small animals.
Coordinative Chain Transfer Polymerization: Recent Advances and a new Paradigm using rare Earth Catalysts

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Coordinative Chain Transfer Polymerization (CCTP) has gained much interest these last years1-7 due notably to its potentialities for molecular weight control and atom economy, for polymer functionalization and for its aptitude to create original microstructures. The process depicted Scheme 1 involves the use of a transition metal catalyst and a main group metal alkyls as chain transfer agent (CTA). If the transmetalation between the transition metal and the main group metal shows a rapid and reversible character, and involves all alkyl groups of the CTA in the absence of other termination reactions, the polymerization is known as a Catalyzed Chain Growth (CCG) or Aufbau reaction. CCG are particularly interesting reactions, as they allow controlled and living polymerizations which can in addition be stereoselective due the presence of the transition metal catalyst.

Scheme 1. Coordinative Chain Transfer Polymerization (CCTP). Polymer* represents a growing polymeric chain, M the transition metal allowing propagation, L a ligand and CTA the chain transfer agent used in excess.

Using the borohydrido half-lanthanidocenes Cp*Ln(BH₄)₂(THF)₂ (Ln = Nd, La; Cp* = C₅Me₅) combined to magnesium dialkyl as CTA, we reported the first examples of polystyrene⁴ and polyisoprene⁵ CCG. Factors affecting styrene insertion vs. βH elimination are discussed using additional experimental results obtained with the rare earth trisborohydrides Ln(BH₄)₃(THF)₃ (Ln = Nd, La) and the lanthanum trichloride LaCl₃(THF)₃. The regioselectivity of the polymerization of isoprene can be fine-tuned using combinations of magnesium and aluminum alkyls, enabling the unprecedented 1,4-trans stereospecific CCTP of isoprene. The application of CCTP to the statistical copolymerization of both monomers for different CTA/catalyst ratio enables an unexpected control of the composition of the resulting copolymer, highlighting a new concept for this purpose.⁷;⁹ We show that the apparent comonomer reactivity can be controlled similarly in the course of styrene/hexene statistical copolymerizations, extending the range of application of the new paradigm.

Activation and Functionalization of CO₂ and Related Heteroallenes at Reactive Uranium Complexes

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The tris-aryloxide triazacyclononane ligand, ((t-Bu, t-BuArO)₃tacn)³⁻, and its sterically more demanding neopentyl, adamantyl and diamantyl derivatives have provided access to reactive coordination compounds of uranium in oxidation states III, IV, V and VI and custom-tailored environments. These complexes display a pronounced reactivity towards small molecules of biological and industrial relevance. Reactions are presented that result in carbon dioxide coordination, activation, splitting and functionalization. Newly developed chelators and their reactive chalcogenide-bridged U⁴⁺(μ-E)U⁴⁺ (E = O, S, Se) complexes are introduced and an outlook into their reactivity towards CS₂ and COS is given.

Two-photon Sensitized Lanthanides Luminescence: Bio-imaging Applications from the Green to the Infra-red

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In the last decade lanthanide complexes have been extensively used for their catalytic, magnetic, luminescence properties for applications ranging from material sciences (Laser, color screen, telecommunication devices…) to biological imaging (MRI contrast agent, fluoroimunoassay…). By contrast, the study of the nonlinear optical (NLO) properties of lanthanide remains in its infancy and becomes currently an emerging field of research.¹

In this context, the sensitisation of lanthanide luminescence in the green (Tb),² red, (Eu)³ even infra-red (Yb)⁴ has been achieved by a two-photon antenna effect, a third order NLO phenomenon. Optimisation of the molecular two-photon cross-section involving a new sensitisation process, design of Ln-based nanoparticles as well as applications in bio-imaging using confocal biphotonic microscopy will be presented.⁵

4. Unpublished results
Reduction of Cp₂MCl₂ (M = Ti, Zr) by Lanthanides: Towards new Applications in Organic Synthesis

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Multimetallic systems have found widespread applications in organic transformations.¹ Rare earth metals are interesting partners in such systems due to their hard Lewis acidity and their rich coordination chemistry. In addition, the lanthanide contraction opens up the possibility of fine tuning reactions.

In recent years, it has been shown that the reduction of Cp₂ZrCl₂ with lanthanum or Mischmetal generates a new divalent zirconocene equivalent [Cp₂Zr-LnCl₃] with various applications in organic synthesis.² In combination with AlCl₃, this system gives access to new catalytic transformations.²c,d

We report here our ongoing investigations on the reduction of group 4 metallocene complexes using the whole series of lanthanide elements. A comparison between titanium- and zirconium-based complexes is drawn and the outcome of electrospray mass studies is discussed. New applications of the Cp₂MCl₂/Ln system in organic synthesis are also presented.

New rare Earth and Alkaline Earth Metal-boron and Metal-metal Bonds

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The development of hitherto unknown or unexplored metal-element bond partners (metal-non-metal or metal-metal interactions) is an area of intense current interest in rare earth chemistry. Transition metal boryl compounds (L)M(BX₂)ₓ, containing 2-center, 2-electron σ-bonds have been a topic of outstanding interest for the past 20 years, mainly due to their pivotal roles in a variety of catalytic and stoichiometric transformations.[1] In the first part of this presentation we will report on the synthesis and electronic and molecular structures of the first f element boryl compounds, as summarised in Figure 1.[2]

Fig 1. Compounds with Sc–B, Y–B Lu–B σ bonds; representation of the HOMO (Ln = Y).

We have also recently been interested to make comparisons between divalent rare earth and alkaline earth elements in metal-metal bonding, a topic of renewed recent interest across all the principal blocks (s-, p-, d- and f-) of the periodic table.[3] Figure 2 summarises some of the Yb-Fe and Ae-Fe bonded (and non-bonded) compounds we have recently prepared and structurally characterized. The synthesis and molecular electronic structures of these will also be reported.[4]

Fig 2. Compounds with (and without) Ln–Fe and Ae–Fe bonds.

References
The Potential of High-resolution X-ray emission and Resonant Inelastic X-ray Scattering Techniques for Speciation studies of Actinide Materials

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High resolution X-ray emission spectroscopy (HRXES) [1, 2] and non resonant inelastic X-ray scattering (NIXS) [3] combined with quantum theoretical tools are gaining importance for understanding electronic and coordination structures in various materials. Applying these techniques, our understanding may one day reach levels high enough to predict reactivity and physical behavior of the actinide elements. HRXES is successfully used to remove lifetime broadening by registering the partial fluorescence yield emitted by the sample, thereby yielding highly resolved X-ray absorption spectra (PFY-XAS), which often display resonant features not observed in conventional XAS. Resonant X-ray emission spectroscopy can be applied to obtain bulk electron configuration information, in solids, liquids and gases. NIXS is extremely suitable for electronic structural studies of actinide materials, e.g., in in-situ investigations.

The HRXES and NIXS techniques will be outlined and their advantages compared to standard XAS. Example U L3 and M5 edge studies of uranium in different oxidation states [1, 3], U6+ in different minerals, polarization dependent investigations of uranium containing single crystals and uranium sorbed on magnetite nano-particles will be shown. Experimental results are supported by ab initio calculations (DFT, FDMNES, FEFF9).

Rare earth metals (REMs) can be produced from their different compounds (oxides or halides) by metallothermic or electrolytic processes. Electrolytic methods usually imply lower cost, but higher purity is often achieved by the metallothermic ones.

There are not reliable sources describing accurately today’s production processes for the different REMs. However, it is believed that the largest quantity of REMs commercially produced throughout the world is obtained by electrolytic methods using either fluoride or chloride electrolytes [1].

Experts in the field point out that industrial production of most of the REMs in China is done by electrowinning from fluoride melts, using RE oxides as raw materials (e.g. Nd). Sm is however produced by calciothermic reduction and subsequent vapour phase distillation [2].

It is well known that electrowinning in the liquid state has several advantages: i) facilitates the elimination of salt remains in the cathode product; ii) minimizes contamination of the reduced metal; and iii) enables continuous operation and high volume levels of production. However, this is a challenge in the case of electrolytic production of heavy RE elements due to their high melting points and vapour pressures. In this case, the product recovery might be facilitated by using cathodes which form liquid alloys with the deposited REMs. Examples of such cathode materials can be liquid Cd, Mg or Zn, or solid Fe, Mn or Co.

In this presentation, an overview of the electrolytic processes for REMs and alloys from molten salts will be given. The challenges related to these processes will be described and possibilities for research opportunities will be suggested.

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Uranium Complexes Featuring U=C Double Bonds

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By comparison with the considerable amount of work devoted to the carbene complexes of d transition metals, the chemistry of such compounds with f-elements remains largely underdeveloped. Because lanthanide and actinide ions are not expected to stabilize carbene ligands by π-back-donation, unconventional routes to the synthesis of carbene complexes must be explored to prepare species featuring an f-element metal-carbon double bond. In this perspective, geminal dianions are attracting much attention, since the coordination of a dianionic carbon center to an oxidized metal center results in the establishment of a metal-carbon double bond.1

Exploiting the reactivity of the bis-diphenylthiophosphinoyl-methanediide dianion, we have synthesized a series of uranium carbene complexes with different coordination environment and redox states (U⁴⁺ and U⁶⁺).2-4 Using a joint theoretical/experimental approach, the bonding schemes in these complexes has been explored and compared to their zirconium analogues, to unveil the specific bonding interactions at stake in uranium carbene complexes. Along with the synthetic aspects, we will discuss how the nature of the U=C double bond is influenced by changes in the coordination sphere of the uranium ion.

Lanthanide(III) Complexes of some Natural Siderophores: Thermodynamic, Kinetic and Relaxometric study

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The Magnetic Resonance Imaging (MRI) is one of the most important non-invasive diagnostic tools widely used in modern clinical practice. As a result of the intensive research conducted in the past 25 years 9 Gd(III) based complexes were approved for in vivo applications as Contrast Agents (CA) in MRI. In order to prevent the toxic side effects of the Gd(III) ion it is usually sequestered by using multidentate ligands bearing acetate, phosphonate, phosphinate, alcoholic OH or amide pendant arms.[1] However lanthanide(III) complexes formed with organic ligands incorporating hydroxamic acids residues were not studied in detail, although chelators belonging to this class of ligands such desferrioxamine B (DFB) or desferricoprogen (DFC) have already been used for treatment of chronic iron overloads or more recently even for sequestering radioisotopes such as 89Zr.[2]

We have determined the speciation and stability constants of the complexes formed in Ln:DFB and Ln:DFC systems for the Nd3+, Gd3+ and Yb3+ ions by using pH-potentiometric method. The equilibrium in these systems can be described by considering LnL type complexes, but in both cases dinuclear complexes of low stability were also detected. The stability constants for the Ln(DFB) complexes are in the range of 12.58 (Nd3+) - 15.28 (Yb3+), while the stability constants of the Ln(DFC) complexes are being considerably higher (14.42 (Nd3+) - 16.49 (Yb3+)). This result is very likely a consequence of longer connecting chains between the -C(=O)-N(-OH)- moieties associated with the effect caused by the presence of the double bonds in β position to the hydroxamic residue. The stability of the complexes are still being much lower than those of LnL3 type complexes of some aromatic hydroxamic acids (e.g. 2-hydroxyquinoline-N-oxide or benzohydroxamic acid) indicating that the relatively long spacer between the hydroxamic acid moiety is unfavorable for the Ln3+ complexation.[3] The relaxometric and the kinetic study was conducted for the Gd(DFB) complex. Our data revealed an interesting pH dependence of the relaxivity associated with large hydration number and fast water exchange, which is favorable for the complexes considered in CA research. However the Gd(DFB) complex was found to be kinetically labile as it dissociates within 5 ms in the presence of Cu(Cit)2- complex near physiological pH and hence can't be suggested for in vivo applications.


Acknowledgement
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New Discrete 3D Complexes with Lanthanides. Design of Supramolecular Nanocapsules

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Our research is focused on the design, synthesis and characterisation of new polynuclear complexes, which may find applications in medical imaging, bioanalytics, molecular sensing, and nanomaterials. In this context, the study of lanthanide-containing systems is a natural choice, since Ln(III) cations exhibit quite similar thermodynamic behaviour, but possess rather different luminescent and paramagnetic properties along the series. Therefore, the incorporation of several lanthanides (identical or different) in a single supramolecular complex may provide interesting functionalities.

Recently, we have designed and prepared new organic tripodal receptors for building polynuclear systems. Indeed, the lanthanide-mediated self-assembly processes provide tetranuclear1 and pentanuclear2 edifices with 3D arrangement of metal ions, whose structures and physico-chemical properties will be discussed in this contribution. Moreover, some of these supramolecular systems contain an inner cavity, which allows to selectively accommodate anionic analytes.3,4 The host-guest interactions can be further tuned through the ligand structure, which also defines the cage size.

Structure, Magnetic Properties and Redox Reactivity of Schiff Base Complexes of 4f and 5f Elements

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The redox chemistry of actinides plays a crucial role in many aspects of nuclear technology including nuclear fuel design, reprocessing and safe disposal and in determining the mobility of actinides in the environment. Moreover the unconventional properties and reactivity of lanthanides and uranium compared to d-block metals could lead to future applications in catalysis and material science. Schiff bases are easy to synthesize, highly π-delocalized ligands that can stabilize metals in different oxidation states. Such redox-active ligands also provide a convenient way to store electrons in metal complexes through metal assisted reversible reductive coupling of the imino groups. Surprisingly the use of such Schiff base ligands in f element chemistry has mostly been limited to the chemistry of uranyl(VI) and trivalent lanthanides. We have recently shown that multidentate Schiff bases can be used to stabilize uranium in the elusive pentavalent oxidation state.\(^1\) Thus, a series of complexes of pentavalent uranyl of different nuclearity has been prepared using polydentate Schiff bases. Recent reactivity studies of such uranium compounds shed light on the mechanism of disproportionation of pentavalent uranyl and afford new polynuclear complexes with interesting magnetic properties.\(^2\) \(^3\) The reactivity of Schiff base complexes of UO\(_2^+\) with different cations leading either to disproportionation or to new original polynuclear assemblies will be presented.

We have also shown that the tetradeinate Schiff base salophen can be used to stabilize reduced uranium and lanthanide complexes by storing electrons in C-C bonds formed by reductive coupling of the imino groups.\(^4\) The stored electrons can become available to oxidizing agents through cleavage of the C-C bond. The reductive coupling of the Schiff base yields dinuclear uranium complexes well suited for the study of magnetic interaction and reactivity. The structure, reactivity and magnetic properties of these complexes will be presented.


Designing Water Soluble Lanthanide Complexes with double Sensitization Ability

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A flexible framework allowing the design of multimodal water soluble ligands for trivalent lanthanide ions is discussed here. The structure of the ligand encloses three moieties. The first part is a dipicolinate coordination site that yields highly stable tris complexes and that possess good photophysical properties for the sensitization of a luminescent lanthanide ion under short wave UV (middle UV, below 300 nm). The second component is a fluorophore that further extends or modulates the absorption of the complex, that exhibits its own fluorescent emission, and that may also act as a sensitizer of a lanthanide ion. The third moiety is a polyoxyethylene linker, which binds the first two parts together, controls the distance between the lanthanide ion and the additional fluorophore, and increases the water solubility of the complex. Some coumarin derivatives are investigated here as different fluorophores and show that considerations other than the energy of the triplet state need to be taken into account in the design of distant sensitizers. This framework also enables the investigation of the distance dependence on the sensitization efficiency. The sensitization is indeed often assumed to occur through a Förster’s or a Dexter’s mechanism, and thus to have a strong correlation to the separation distance between the donor fluorophore and the acceptor lanthanide ion. However, few reports from literature are expressly demonstrating this relationship. We intend here to briefly present the synthesis of such ligands and discuss the photophysical properties of their complex.
Lu₂O₃ Sesquioxide Nanostructures for Photonics Applications

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Cubic Ia-3 Lu₂O₃ is a widely used material for laser and photonic applications due to the advantageous conjunction of excellent thermo-mechanical properties, high refractive index, relatively low phonon energies, and high doping admittance for optically active trivalent lanthanide (RE) cations. Furthermore, doping with RE cations in this host shows high optical absorption and emission cross-sections as well as large crystal-field splitting [1]. Different Lu₂O₃ based photonic materials in nanocrystalline forms (nanocrystals, core-shell structures and nanorods) have been produced exploring new optical properties derived of the size reduction.

Nanocrystalline RE-Lu₂O₃ particles were produced by the Pechini method [2]. These could be used as precursors in the fabrication of transparent laser ceramics through dense sintering [3]. The use of ceramics as an alternative to single crystals is justified in some compounds, in which the crystal growth is difficult and has a high cost. Furthermore, the ceramics show better thermo-mechanical properties, such as the thermal shock parameter and resistance to the laser damage [4].

Nanostructured SiO₂@RE:Lu₂O₃ core-shell particles were produced by a modified Pechini using ~260 nm amorphous SiO₂ microspheres [5]. The development of SiO₂ based core-shell structures, has gained the interest in photonics due to the possibility of obtaining spherical phosphor particles with high packing densities and low scattering of light [6].

RE doped nanorods (NRs) have been prepared through a soft hydrothermal procedure with a diameter of approximately 90 nm [7]. Given the special interest of 1D crystalline nanostructures, RE doped nanorods could play an important role as functional building units for the fabrication of nanodevices based in 2D or 3D ordered structures.

Actinide Polysulfides in the Gas Phase

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The actinide (An) sulfides have interesting electronic properties which may reveal insights about covalency, especially for early actinides. Sulfur is an important element in the nuclear field as a donor atom of ligands used in actinide separation processes and in selective sulfurization of rare earths in spent fuel reprocessing. Although very little information is available on the thermochemistry of An sulfide molecules, we have recently investigated experimentally and theoretically the energetics of AnS species [1].

An polysulfides were obtained in the gas phase by reacting singly- and doubly-charged An metal ions, from Th to Cm, with COS, using Fourier transform ion cyclotron resonance mass spectrometry (FTICR/MS).

The An⁺ and An²⁺ yielded families of mono- and di-cationic species, respectively. In the cases of Th⁺ and U⁺ ions, sequential formation of polysulfide species was observed from the monosulfide up to the trisulfide, ThS₃⁺. With Th²⁺ and U²⁺, we observed also the formation of the tetrasulfide, ThS₄²⁺ (Fig. 1).

Most of the AnSₙ⁺/₂⁺ ions also reacted with COS to give oxide and oxosulfide ions.

Computational studies (DFT and CCSD(T)) of the singly and doubly charged Th and U polysulfides showed that the structures are mostly of the metallacycle type. For example, US₂²⁺ is quite different from linear uranyl, O=U²⁺=O [2], with the bent isomer ≈ 100 kJ/mol lower in energy than linear thio-uranyl, S=U²⁺=S.


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The use of supported catalysis is increasingly widespread in chemistry because of its specificity compared to the heterogeneous and homogeneous catalysis. Grafting catalysts on a surface leads to heterogeneous catalysts with well-defined active sites. However, it is hard to address experimentally the grafting mode of the catalyst complex. Theoretical methods can be used in order to give some insights into this problem. In a first part of this talk, we will define the most pertinent model of the surface exhibiting different silanol groups. The silanol groups, which come from the deshydroxylation reaction of the silica surface, are very reactive and will be involved in interactions and chemical reactions at the silica surface. The nature of the thermic treatment of the silica (300 or 750°C) will be considered in the modelling and different models will be proposed. Then we will consider different grafting modes of the lanthanide complex on the silica surface, and give some reactivity results on the polymerization of ε-caprolactone and MMA.
The report presents the main results on the investigations of the chemistry and the small scale production of rare earths (RE) performed (1985-2010) in the Department of Inorganic Chemistry, Sofia University, in the fields of (i) RE recovery from waste materials, (ii) RE separation and production of high purity oxides, (iii) mechanochemistry of the RE, (iv) RE based materials and (v) thin film preparation. Some of the main results can be summarized as follows: (i) proposed methods for synthesis and purification of RE silicates; (ii) developed methods for recovery of RE from waste and by-products; (iii) registered mechanochemical effects on RE oxides and proposed mechanochemically assisted methods for synthesis of RE silicates and diketonates; (iv) elucidated the chemical nature of solid RE complexes with ethylhexylphosphoric acid and their application for La separation; (v) clarified the chemistry of processes involved in the polymerized complex method, applied for preparation of RE-based compounds; (vi) proposed spray-pyrolysis deposition of thin films using mixed-metal citrate complexes; (vii) realized synthesis and immobilization of RE diketonates in different matrices; (ix) studied the influence of RE on the photocatalytic activity of TiO₂; (x) developed production routes for some RE compounds and carried them out in practice; (xi) synthesis, characterization and investigation of the optical and pharmacological properties of RE complexes with some coumarin derivatives.

References
Coordination and Photophysical Properties Homo- and Hetero-metallic Complexes, Multimodal Imaging Agents

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The photophysical properties of trivalent lanthanides make their complexes particularly suitable for the development of fluorescent probes for biomedical applications and for the design of optical devices (sensors, light emitting diodes, solar cells, lighting). To date there is a strong interest to shift the emission of the probes or devices components in the low energies and use the near infrared area to increase their performance. The development of efficient architectures for the sensitization of the luminescence of lanthanide ions emitting in the near-IR range, remains an important challenge and performance of the existing systems could be significantly improved by a better design of the molecules employed to chelate lanthanide ions. Progress in optical devices in the NIR depends on the development of the excitation in the visible with combining high stability of the systems, high sensitisation, and high quantum yields.

Here we present an overview of the work developed in our laboratory the rational approaches and the strategies. We will present synthetic strategies to selectively introduce lanthanides into polymetallic luminescent assembly, the optimisation of the sensitization of visible and NIR lanthanide emission, the optimisation of the coordination properties and luminescence of NIR-emitting lanthanide ions grafted on semiconductor nanocrystals (quantum dots) or encapsulated in silica nanoparticles. Moreover the energy transfer processes in these systems and homo- or hetero-metallic edifices containing lanthanide will be established. The evaluation and studies of the potentialities of the developed Ln-based optical devices for application in in-vivo NIR imaging and in other fields such as fluorescent labels, light-emitting diodes (LEDs) and solar cells will be presented.

Group Separation of Heavy Metals followed by Subsequent and Individual Separation of Lanthanides by Chelation Chromatography

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Abstract: This article provides an alternative method for group separation of heavy metals (HM) from rare earth elements (REEs) followed by online individual separation of REEs using a strong sulfonated polystyrene resin, Dowex 50W-X8, 200-400 mesh. Various chelating agents were used as the mobile phase such as diethylenetriaminepentaacetic acid (DTPA), 2,6-pyridinedicarboxylic acid (PDCA), nitrilotriacetic acid (NTA), α-hydroxyisobutyric acid (HIBA) and oxalic acid. These chelating agents were selected with different numbers of carboxylic acid groups and various geometrical structures which control the elution capability as well as the separation efficiency. Effective key parameters were studied such as eluent type, concentration, pH and flow rate. The results showed that selective group separation of HM from REEs could be done by different options including 0.0005 M PDCA at pH 1, 0.005 M DTPA at pH 2, 0.1 M HIBA at pH 2 or 0.0007 M NTA at pH 2 while oxalic acid showed poor group separation of HM from REEs. The selective elution of HM is attributed to strong complex formation between the carboxylic acid groups of the chelating agent with divalent metal ions more than trivalent ion especially at relatively low pH values. NTA chelating agent was selected for further investigation to test the individual separation of REEs. Finally, the optimum chromatographic conditions showed that HREEs and IREEs could be efficiently separated by 0.001 M NTA at pH 3 while LREEs have been separated by 0.005M HIBA at pH 4 followed by 0.001M PDCA at pH 2.

Keywords: Separation of heavy metals, rare earth elements REEs, chelating ligands, Dowex 50.

0.0007 M NTA pH= 2 (0-49) F.R 40 + 0.001 M NTA pH 3 (50-179) F.R. 10 + Water (180-182) +0.05 AHIBA pH 4 FR 10 (183-213 +Water (214)+ 0.001 PDCA pH 2 FR 15 (215-271). 20 REEs, 3 µm
Bond activation Chemistry with rare-earth Metal N-Heterocyclic Carbene Complexes

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Many organometallic f-block complexes are highly effective at the activation of small molecules, although the subsequent functionalisation chemistry can be hampered by the absence of readily accessible redox chemistry for these metals. We have been studying ligand systems that might supply such electrons, or bring in a second substrate.

We will present new f-element adducts of polydentate tethered N-heterocyclic carbene ligands. In contrast to softer metal NHC complexes, the carbene group in complexes such as 1 and 2 is more labile and hence more reactive in these systems.

We will show how upon labilisation, the pendant carbene can work in tandem with the Lewis acidic metal to attack small molecules such as carbon oxides and oxygenates, organic azides, phosphines and boranes. We will also show how these and related, f-block systems can participate in the activation of other inert small molecules and discuss our progress towards developing catalysed C-H cleavage and C-C bond forming reactions by f-block complexes.

\begin{scheme}
\begin{align*}
1 & \quad 2 \quad 3 \quad \text{ER} = \text{O, NR}
\end{align*}
\end{scheme}

References

Infrared spectroscopic observations in an argon matrix are reported for eight new LnCO species with Ln = Pr, Nd, Sm, Eu, Tb, Dy, Ho and Er. Isotope substitutions are done for C(12/13) and O(16/18). Theoretical calculations are performed for the entire series at DFT level. Specific cases are also investigated at CASPT2 level. The covalent M-C bonding contains both C → M σ donation from the carbon lone pair and M 5d → CO 2π* back donation contributions. The total spin may have contributions from the 4f, M ‘σ doughnut’, and π orbitals. The M-C bond can approach a double bond in strength. Towards the end of the Ln series it becomes very weak. Empirical correlations are found between the C-O stretch frequencies and the atomic excitation energies to a 6s^25d^1 state, or to the boiling points of the M.

As a general conclusion, little information is available on bonds between electropositive ligands and formally zero-valent Ln. We also relate the atomic trends of the Ln valence orbitals 6s and 5d to those of their transition-metal neighbours.

Rib Waveguides Fabricated by fs-laser Ablation on (Yb, Nb):RbTiOPO₄/ RbTiOPO₄ Epilayers

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The crystals of the KTiOPO₄ (KTP) family are interesting nonlinear optical materials due to its excellent properties. They have high nonlinear optical coefficients, high laser damage threshold, high chemical stability, accompanied by a wide range of wavelength acceptance, which make them very useful for Second Harmonic Generation (SHG). RbTiOPO₄ (RTP) belongs to the KTP family and presents an extra advantage in front of KTP: it can be doped with lanthanide ions with higher concentration than KTP, with the possibility to obtain a self-frequency doubling (SFD) material. Among the lanthanide ions, Yb³⁺ has special interest because of its emission at around 1 μm, with only two energy levels, its low quantum defect and high lifetime. The co-doping of RTP with Nb⁵⁺ and Yb³⁺ allows increase the coefficient of distribution of Yb³⁺ in the RTP structure to levels useful for lasing.

We grew epitaxial layers of (Yb,Nb):RTP/RTP by the Liquid Phase Epitaxial Method (LPE) to fabricate planar waveguides with enough large optical paths.

The LPE growth was made using self-flux solutions to avoid the incorporation of foreign ions in the crystal structure. The epitaxial growth was carried out at a temperature 2 K below the saturation one, for 2 h and the substrate rotation was 40 rpm. The chemical composition of the epilayer, obtained the Electron Probe Microanalysis was RbTi₀.₉₇₁Yb₀.₀₁₅Nb₀.₀₁₄OPO₄.

The channels were fabricated using a pulsed fs-laser amplification system (shown in Figure 1) with 1 KHz repetition rate and pulse duration of 120 fs. The output energy was 1 mJ and the central wavelength was 799 nm. A spatial light modulator was used to control the beam wavefront, allowing us to design the intensity of the profile of the focused beam. To improve the quality of the channels, we used the approximation scanning method. The focused beam was multiplexed in seven spots and each spot rewrites the channel written by the previous one, but with a slight displacement.

Numerical simulations of the light confinement at 632 nm show confinements very close to 90%. The channel waveguide modes were excited at the same wavelength and the near field pattern, observed with a CCD camera, shows a Gaussian profile (see Figure 2).

The transmission losses in the waveguide were around 2.5 dB/cm. Finally, Type II Second Harmonic Generation in these waveguides, from a fundamental radiation of 1137 nm, was obtained.
POSTERS
Chemical Sensitization of Lanthanide Luminescence: A New Road

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The development of luminescent signalling systems is highly topical in supramolecular chemistry.¹ On the other hand; the development of sophisticated reporter probes for in vivo imaging of anatomy and physiology has become a very active field of research.³

Herein we wish to report the synthesis and properties of a novel supramolecular lanthanide complex 1, in which, the lanthanide luminescence could be sensitized chemically.

References

Lanthanide complexes have been widely used in a variety of applications such as imaging and assay related ones.\(^1\) In particular, the incorporation of luminescent lanthanide complexes in solid matrices with a well defined structure has recently attracted considerable attention in materials science.\(^2\)

Herein we describe the synthesis and properties of some novel macromolecular lanthanide complexes.

**References**

The development of molecular magnetism has led to the discovery of a new class of materials, where individual molecules are able to function as magnets, the so called single-molecule magnets (SMMs). SMMs are characterized by a slow relaxation of the magnetization below a certain blocking temperature and may have important potential applications in data storage and quantum computing. This behaviour was first observed for polynuclear aggregates of paramagnetic transition-metal ions, in particular manganese-oxo clusters, but in 2003 Ishikawa et al. found out that mononuclear lanthanide bis-phthalocyanine compounds exhibited SMM behaviour as well. More recently a few actinide-based SMMs have also been identified.

In this communication we present the study of the magnetic properties of some uranium(III) complexes based on the hydrotris(3,5-dimethylpyrazolyl)borate ligand (TpMe2), directed to probe the exchange interactions and slow magnetic relaxation behaviour in detail. AC and DC magnetization measurements, at different temperatures and under variable applied magnetic fields, revealed a frequency dependence of the magnetization, characteristic of SMM behaviour, which depends on the ligand and coordination environment.

Tm-doped Waveguides for Integrated Photonic Devices

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Laser generation in active crystalline composites is of interest because of the challenge of integrating photonic components into smaller devices. Among all materials studied, the monoclinic rare-earth double tungstates doped with an active ion grown on a crystalline substrate of the same family have been a subject of work for two ions, Yb (1 µm) [1] and Tm (2 µm) [2].

The motivation of the current work was to improve the efficiency of the laser generation in such Tm-doped planar waveguides operating at 1.8 µm. For this, two planar waveguides grown on the (310) and (010) faces of the KYW substrate were considered and compared.

The monoclinic double tungstates show natural faces labelled in figure 1a. The layers we used for the laser experiments were 10 µm (010) and 11 µm (310) thick and an optical path of 5 mm. The active layer on the (310) face operated in cw regime delivering a maximum output power of 28.7 mW at a maximum absorbed power 53 mW at 1884 nm polarized parallel to Np. The laser threshold amounted to an absorbed power of 14 mW. Figure 1b shows the output-input laser characteristics for the layer grown on the (310) face.

The laser experiment with the active layer grown on the (010) face could not operate in cw regime due to thermal problems. The use of a mechanical chopper (50% duty cycle) enabled laser generation with around 1 mW average output power showing polarization switching from the threshold operating simultaneously at 1826 nm (Np) and at 1832 nm (Nm) as can be seen in figure 1c.

The big difference in laser performance for the two cases can only be attributed to the strong dependence on the thermal conductivity for all direction in each sample. In reference [3], was studied the thermal conductivity tensor of the monoclinic double tungstate crystals giving answer for the phenomenon we demonstrate here.

Synthesis and Reactivity of the U(IV) bis(C,N)metallacycle [M][U(N*)(κ²-CH₂SiMe₂N{SiMe₃})₂] (M = K, Na, Li). Access to high-valent Species

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The bis(trimethylsilyl)amide ligand (N* = N(SiMe₃)₂) is ubiquitous in coordination chemistry. It is able to stabilize metal centres in their lowest and highest oxidation states and can be substituted with proton acidic molecules, so that bis(trimethylsilyl)amide compounds are valuable starting materials for inorganic and organometallic syntheses. In the presence of a base the “MXN*” complexes are often transformed into metallacycles [M(κ₂(C,N)-CH₂SiMe₂N{SiMe₃})] following γ-CH deprotonation and HX elimination.

We present the formation of the title compound from UCl₄ and the synthesis of the (O,N) derivatives obtained from CO and CO₂ insertion into the sole U–C bond. Oxidation of these complexes with I₂ revealed distinct behaviours, leading to a novel U(IV) mono metallacycle or U(V) derivatives. Their treatment with the N₃⁻ and CN⁻ anions is presented.

Conditions were found which permit the use of UCl₄ instead of the less convenient borohydride starting material U(BH₄)₄ to prepare the mono-, bis- and tris- uranium(IV) carbene complexes with the dianionic ligand [C(Ph₂PS)₂]²⁻ (SCS²⁻) (Fig. 1). The species [Li(THF)₂U(SCS)Cl₃(THF)], [U(SCS)₂(THF)₂] and [{Li(OEt₂)}₂U(SCS)₃] proved of interest for developing the carbene chemistry of U(IV), as illustrated with the synthesis of carbene compounds with cyclopentadienyl and cyclooctatetraenyl ancillary ligands.

The weakly reducing anions shown in Fig. 1 were also useful for the synthesis, directly from uranyl UO₂X₂ precursors, of rare stable organometallic uranyl complexes featuring single and double uranium(VI)–carbon bonds.

Density functional theory analyses of these U(IV) and U(VI) complexes showed that the U–C and U=C bonds are polarized toward the nucleophilic carbon.

Lead(II) compounds, especially cyclopentadienyl derivatives of type PbCp\textsubscript{R}\textsuperscript{2} (Cp\textsuperscript{R} = C\textsubscript{5}Me\textsubscript{5}, C\textsubscript{5}Me\textsubscript{4}Et, C\textsubscript{5}H\textsubscript{3}(SiMe\textsubscript{3})\textsubscript{2-1,3}), act as easy-to-synthesize precursors for oxidative ligand transfer reactions when exposed to divalent rare-earth metal complexes.\textsuperscript{1} The target molecules in these protocols are usually the sterically crowded homoleptic complexes LnCp\textsuperscript{R}\textsubscript{3}. A similar attempt, aiming at the homoleptic \textsuperscript{-diketiminato complex \[\text{YbL}\textsubscript{3}\] (L = \{[N(SiMe\textsubscript{3})C(Ph)]\textsubscript{2}CH\}) via the reaction of PbL\textsubscript{2} with \[\text{YbL}\textsubscript{2}\], led to the expected oxidation, but as well to a sterically induced self-deprotonation of the ligand.\textsuperscript{2} Not only organolead(II) complexes can be used as oxidation agents, but also Pb(II) salts like PbF\textsubscript{2}, affording heteroleptic compounds such as Ln(Tp\textsuperscript{Me,Me})\textsubscript{2}F.\textsuperscript{3} In general, the resulting trivalent rare-earth metal complexes can be obtained in high purity and high yields. In this study, the Pb(C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}-based Ln(II)→Ln(III) oxidation protocol has been exploited for the synthesis of a series of heteroleptic trivalent rare-earth metal complexes.

Figure 1. Solid state structure of (C\textsubscript{5}Me\textsubscript{5})Yb[N(SiHMe\textsubscript{2})\textsubscript{2}](thf).

References


The demand for biodegradable polyesters is nowadays constantly increasing, owing to the numerous high-technology applications in biomedical and pharmaceutical fields.\textsuperscript{1} Such polymers are generally produced by ring opening polymerization and since the last two decades, a growing number of studies involving rare earths compounds as initiators have been reported.\textsuperscript{2}

Despite the fact that samarium diodide is known as the famous versatile reagent for organic chemistry, divalent samarium and more generally divalent lanthanide compounds have been much less studied in the frame of polymerization catalysis and only a little number of reports regarding the ROP of lactones, but with no mechanistic aspects, can be found in the literature.\textsuperscript{3}

By view of our experience in the synthesis of lanthanide borohydrides and their applications in polymerization,\textsuperscript{2,4} we turned our attention towards Sm(BH\textsubscript{4})\textsubscript{2}(THF)\textsubscript{2} which was mentioned in the literature but was not characterized otherwise than by IR spectroscopy.\textsuperscript{5}

In this contribution we will present the synthesis of samarium\textsuperscript{II} \textsuperscript{6} and thulium\textsuperscript{II} \textsuperscript{7} borohydride compounds, their use as initiators for the ring opening polymerization \(\varepsilon\)-caprolactone \textsuperscript{6,7} and DFT calculations giving insights on the polymerisation mechanism involved.\textsuperscript{8}

Cationic Borohydrido Lanthanide based Catalysts for highly Selective Polymerizations – joint Experimental/Theoretical Approach

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Over the last decade, cationic complexes of the rare earths have emerged as powerful species in polymerization catalysis. However, despite their efficient and selective behavior, particularly towards olefin or conjugated diene polymerization, a major drawback is their very high sensitivity which renders them hard to handle and isolate. Moreover, they are mainly prepared starting from highly reactive alkyl derivatives. As an alternative, we focused on cationic compounds of the rare earths issued from the more easily available borohydrides as precursors.

In this contribution we will present some examples of borohydrido rare earths (Nd, Sc) based cationic complexes that can be activated by in situ alkylation, to generate efficient catalysts for the stereoselective polymerization of isoprene and styrene. In particular, when the half-scandocene Cp*Sc(BH4)2(THF) is employed as precursor, the resulting catalyst allows both the selective cis-1,4 polymerization of isoprene and the purely syndio specific polymerization of styrene.

Copolymerization results and the molecular structures of borohydrido rare-earths based pre-catalysts will also be presented. The high cis-selectivity towards isoprene polymerization has been rationalized in a theoretical study, this will be included in the discussion.

Multi-electron redox reactions play a key role in many biological and synthetic catalytic processes. Multiple-electron transfer reactions can be achieved from the association of redox-active metal centers and polydentate unsaturated ligands which can store electrons in a reduced form. A particular high current interest arises from the ability of complexes of low-valent f-elements to promote unusual reductive chemistry through unusual reaction pathways, including attractive examples of CO, CO$_2$ and N$_2$ activation. This renders particularly attractive the development of f-elements complexes capable of performing multi-electron reductions. Accordingly, we investigated the association of low-valent uranium and lanthanides (Eu, Nd, Tb, Yb) with non-innocent highly $\pi$-delocalized Schiff bases ligands. This led to the isolation of electron-rich complexes$^[1]$ which are stabilized by storing electrons on the ligands through the formation of C-C bonds. Interestingly, these C-C bonds can be cleaved by oxidizing agents and the electrons released to participate in multi-electron redox reactions, thus providing a unique electron reservoir. The synthesis, structural characterization, electrochemistry and reactivity studies of these new electron-rich f-elements complexes will be presented.

We have been using electrospray ionization quadrupole ion trap mass spectrometry (ESI-QIT/MS) to investigate several aspects of the coordination chemistry of lanthanides (Ln) and actinides (An). These studies range from the characterization of new f-element complexes to the examination of fundamental gas-phase properties of lanthanides and actinides. The experimental studies are accompanied by theoretical calculations of selected systems.

Collision induced dissociation (CID) of $[\text{M(NO}_3\text{)}_x\text{]}^-$ ions is known to yield $[\text{M(O)(NO}_3\text{)}_{x-1}\text{]}^-$ species [1]. In the QIT, CID of $[\text{M(NO}_3\text{)}_4\text{]}^-$ ions, where M = Sc, Y, Ln, produced $[\text{M(O)(NO}_3\text{)}_3\text{]}^-$ for M = Ce, Pr, Nd and Tb (i.e., the Ln with more accessible oxidation state IV), while $[\text{M(OH)(NO}_3\text{)}_3\text{]}^-$ ions dominated for most of the remaining metals (Fig. 1a; hydrolysis results from water in the ion trap); the much smaller Sc yielded both fragment ions. In the cases of Pu, Am and Cm, all having an accessible oxidation state IV, only $[\text{M(O)(NO}_3\text{)}_3\text{]}^-$ ions were observed (Fig. 1b).

Gas-phase reactions with the background water present in the QIT [2] were examined in detail to unravel the diverse behavior of the f-element ions, through the formation of $[\text{M(OH)(NO}_3\text{)}_3\text{]}^-$ by hydrolysis of $[\text{M(O)(NO}_3\text{)}_3\text{]}^-$ ions, and the formation of selected species have corroborated the experimental observations.

Figure 1. CID spectra of (a) $[\text{Ho(NO}_3\text{)}_4\text{]}^-$ and (b) $[\text{Am(NO}_3\text{)}_4\text{]}^-$


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Carbon dioxide is an interesting raw material for the synthesis of carbon containing compounds due to its low cost and abundance. However, it has always been underutilized due to its inert character, the strength of the C=O bonds making it a thermodynamically very stable molecule. In this context, the reduction of CO$_2$ via the use of highly reducing metals is an attractive process. Low-valent f-block elements have especially been of great interest in the last few years. Sm(II) and U(III) complexes have shown their ability to convert CO$_2$ into various products such as oxos, oxalates and carbonates.

In this talk, DFT investigations of experimental reactions between U(III) complexes and CO$_2$, COS and CS$_2$ will be presented. They concern the experimental works of Richard A. Andersen, Karsten Meyer and Geoffrey N. Cloke groups. We will discuss about the particular importance of the steric bulk of the ligands in this reactivity.
Soluble and reactive silylamide complexes, which can be spectroscopically traced (FTIR), are desirable in the study of silica-based surface organometallic chemistry (SOMC) [1]. When targeting a Ce(IV) grafted silica, the synthesis of a complex such as Ce₅[N(SiHMe₂)₂]₆ (L = monovalent ligand; x + y = 4) would be extremely useful. Two synthesis pathways appear possible – a ceric ammonium nitrate/salt-metathesis [2] and a PhICl₂/oxidation approach [3]. In this work, we illustrate both these approaches in the synthesis of the homoleptic complex tetra[bis(dimethylsilyl)amido] cerium (Figure 1).

Figure 1. Synthesis pathways for Ce[N(SiHMe₂)₂]₄.

Computational Studies of the Catalysis of a Fischer-Tropsch Reaction by an Organo-Uranium Complex

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The well known Fischer-Tropsch process is today more than ever a potential solution to counter the decline of fossil fuel as it allows the environmentally friendly formation of hydrocarbons from carbon monoxide (and potentially CO₂) and hydrogen. This process is commonly catalysed by 3d and 4d transition metal catalysts (such as nickel, cobalt, iron and ruthenium)¹ and is still the focus of studies aiming at making it a more efficient process.² In the last few years, Cloke's group has taken advantage of their experience and knowledge of lanthanide chemistry and have put forward the idea of catalysing Fischer-Tropsch process through the use of uranium catalysts. To our knowledge, this compound is at the moment the only diuranium complex capable of facilitating Fischer-Tropsch reactions. However, the mechanism of such reactions is difficult to elucidate through experimental techniques. We therefore apply computational chemistry to this problem.

In this talk, we present computational work done to elucidate the mechanism of a Fischer-Tropsch reaction catalysed by a uranium sandwich complex : \([U(\eta^1-C_8H_6\{Si'Pr_3-1,4\}_2)(\eta^-Cp*)][\eta^1-\eta^-1-C_2O_2].^3\)

Bimodal (MRI/optical) DTPA Bisamide Complexes and their Self-assembly to Micelles

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Magnetic resonance imaging (MRI) is an essential diagnostic tool in various medical procedures. The gadolinium(III) complex of diethylene triamine pentaacetic acid (DTPA) and its derivatives are currently used as in vivo MRI contrast agents. In recent years there is much effort done in order to design contrast agents with improved efficiency and relaxivity, especially at higher magnetic fields. The use of slowly rotating macromolecular complexes causes the relaxivity to increase significantly.1,2 Bimodal contrast agents are gaining increased interest because they can combine the high resolution of MRI with the high sensitivity of optical imaging.3,4 The purpose of the project is to develop luminescent MRI contrast agents which are efficient at strong magnetic fields. DTPA bisamide derivatives containing absorbing aromatic units and C12 or C14 alkyl chains were synthesized and complexes of various trivalent lanthanide ions (Ln = Eu, Tb, Gd, Dy) were formed (see figure). The amphiphilic complexes were incorporated into mixed micelles and their characterization by photon correlation spectroscopy indicated that they were monodisperse and had mean sizes within the same range. The compounds with luminescent lanthanide ions showed very clear emission transitions. The proton longitudinal as well as transverse relaxivities were determined and very favorable parameters were obtained.

Research in the $f$-element Coordination Chemistry lab at the Department of Inorganic and Physical Chemistry of Ghent University (Belgium)

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This poster will give a brief overview of the research topics that are being investigated in the $f$-element coordination chemistry lab of Ghent University (Belgium). As the lab has only been founded in 2008, this research is still quite young and interest in establishing collaborations with interested parties is clearly present.

The research is centered around the synthesis and characterization of luminescent rare-earth containing materials, both classical coordination compounds (discrete mononuclear complexes with organic ligands), metal-organic frameworks, and inorganic nanoparticle systems.1,2

The structural characterization of the synthesized materials is done by single crystal X-ray diffraction on a recently acquired state-of-the-art diffractometer, and via synchrotron techniques such as EXAFS (Extended X-ray Absorption Fine Structure) and HEXS (High-Energy X-ray Scattering).3,4,5

The luminescence measurements are done on a high-end luminescence spectrometer, allowing steady state measurements in the wavelength range of 200 – 5000 nm and time-resolved measurements in the wavelength range 200 – 3100 nm (decay times between 80 ps and several seconds can be measured). The setup also contains a closed cycle cryostat, allowing experiments between 4.2 and 325 K. In addition, an integrating sphere makes the accurate determination of quantum yields possible, both in the visible and the near-infrared. Polarized luminescence can also be recorded.

Synthesis of Intermetallic Nanoparticles Containing f-elements

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Unlike metal alloys, intermetallic compounds (IC) have a crystal structure and chemical formula well defined$^1$. Furthermore, the ICs are mainly known for their magnetic properties and ability to reversibly absorb hydrogen$^1$.

Some techniques were successfully applied to the synthesis of IC nanoparticles containing $d$ transition metals. The best results involve the application of modified polyol process$^{2-4}$ but, the synthesis of IC nanoparticles remains an issue of great importance that in the case of the low temperature IC nanoparticles containing f-block elements is an area that remains virtually unexplored.

Therefore, the purpose of this work was to implement this approach to the synthesis IC nanoparticles containing f-block elements, e.g. LaCu$_2$, LaNi$_5$, SmCo$_5$ or DyFe$_3$. The combination of the unique properties of the f elements with the ability to control the shape and size of the nanoparticles will bring benefits to the expected catalytic properties of these materials. Measurements of XRD, SEM and TEM were performed to characterize the IC. Figure 1 shows TEM and SEM images of some of the IC nanoparticles containing f-elements already synthesized.

![TEM and SEM images of IC nanoparticles](image)

Figure 1— (A) TEM of DyFe$_3$ nanoparticles and (B) SEM of SmCo$_5$ nanoparticles.


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Traditionally, the chemistry of molecular uranium compounds has been dominated by the use of carbon, nitrogen, oxygen and halogen-based ligands. Unlike for the $d$-, $p$- and now even $s$- block, metal-based ligands for uranium are extremely rare and hence little is known about metal-metal bonding in $f$-element chemistry.¹ Given that so few examples of such complexes are reported, considerable potential exists to explore a new territory of actinide chemistry via novel uranium–transition metal complexes exhibiting unsupported heterobimetallic bonds. A range of novel uranium halide, amide and separated ion pair precursors have been synthesised,² as well as an unexpected yet remarkable BPh₄-funcntionalised metallacycle that represents a net double dearylation of BPh₄⁻ and is the first example of its kind to be reported.³ Treatment of these precursors with 1ˢᵗ row (Mn, Fe) transition metal anions and hydrides afforded several bridging carbonyl, solvent separated ion pair and oxo-complexes of uranium,² but none containing the desired U–Mn or U–Fe bonds. However, the U–Ru and U–Re metal–metal bonded complexes [U(Tren₃){RuCp(CO)₂}]⁴ and [U(Tren₃)(ReCp₂)]⁵-⁷ (R = SiMe₃, SiMe₂Bu) have been isolated and structurally characterised. DFT calculations revealed a strong electrostatic $\sigma$- bonding interaction between the U and Ru centres in [U(Tren₃){RuCp(CO)₂}] but a considerably increased degree of covalency to the metal–metal interaction n [U(Tren₃)(ReCp₂)].

Lanthanide doped Submicron-sized Spheres for Temperature Sensing

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With the emergence of ever new applications in microfluidic technology, innovative methods to measure environmental and chemical properties within microchannels are required. Precise control of temperature is a key requirement in many microfluidic applications in biology, in medicine, in electronics and in chemistry¹. In this sense, we devised a novel kind of thermometers with nanometer scaled spatial resolution. These submicrometer spheres of silica are doped with rare earth ions which are capable of accurately determining the temperature of solutions. The behavior of the submicron-sized spheres with the temperature is presented, performed in the physiological temperature range (25–70 ºC).

FIG. (a) TEM micrograph of Tb³⁺ doped submicrometer spheres, (b) Histogram of the height distribution of the Tb³⁺ doped microspheres, (c) dependence of the Eu³⁺ emission with the temperature.

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Uranium(IV) Alkyls for Small Molecule Activation

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Previous work undertaken in this laboratory has demonstrated the remarkable reactivity of U(III) mixed sandwich complexes towards small molecules such as CO, CO$_2$ and H$_2$ at room temperature and pressure.$^{1-3}$ Using the same framework of bulky bis(triisopropylsilyl) cyclooctatetraene ring (COT$_{TIPS}^2$) and pentamethyl cyclopentadienyl (Cp*) ligands, U(IV) alkyl complexes are being investigated to study their reactivity with small molecules. These alkyl complexes undergo insertion reactions with CO and CO$_2$, and form a monomeric uranium hydride species upon exposure to H$_2$, which also shows reactivity towards small molecules. A ‘tethered’ alkyl tuck-in complex involving activation of a methyl group on the Cp* ring also undergoes insertion reactions. Work is underway to fully characterise these complexes and further probe their behaviour.

Strongly-coupled, binuclear uranium oxo complexes from uranyl oxo-rearrangement and reductive silylation

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Uranyl ’Pacman” complexes of the type $\text{UO}_2(\text{H}_2\text{L})_1$, have been known for a number of years and are prepared by the reaction of Schiff-base calixpyrrole macrocycles with uranyl silylamides. The incorporation of a single uranyl dication into this hinged macrocyclic environment has facilitated unique oxo-group reductive functionalization reactions through the incorporation of Group one$^1$ or rare-earth$^2$ metals, and has been used to prepare a diverse range of stable heterobimetallic complexes featuring pentavalent uranyl.

In this talk the first examples of homobimetallic uranyl Pacman complexes are presented, including the new binuclear “butterfly” Pacman complexes $[(\text{R}_3\text{SiOUO})_2\text{L}]_2$ that are prepared by the reactions of 1 with an excess of a uranyl silylamide. These reactions proceed with reductive functionalisation of the hexavalent uranyl to form complexes with two oxo-silylated uranium(IV) centres. Furthermore, a formal rearrangement of the two trans dioxo $[\text{UO}_2]^{2+}$ cations occurs resulting in a diamond or “butterfly” geometry with shared oxo groups. Magnetic susceptibility studies show a strong antiferromagnetic exchange between the two $f^4$ centres at 17 K and computational modelling suggests some retention of multiple U-O bonding. Overall the uranyl bonding in 2 may be considered to be a combination of cis and trans isomers, the former of which has not been previously observed.

Synthesis and Properties of BODIPY-DOTA Dyads

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BODIPY 1 dyes represent an important class of fluorescent dyes due to their unique properties such as sharp fluorescence signal in the visible region with high quantum yield, high stability, good solubility in organic solvents and so forth. On the other hand, the development of sophisticated reporter probes for in vivo imaging of anatomy and physiology has become a very active field of research.

Herein we report the synthesis and properties of some novel lanthanide complexes of BODIPY-DOTA dyads 2 as new supramolecular constructs.

References

Theoretical Insights into the General Mechanism of Formation of the First Vinyl Complexes of U(IV)

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Uranium complexes are capable of producing some of the most extraordinary reactions, which are most of the time impossible to form with other type of metals (e.g. main group, lanthanides or transition metals). This is mainly due to the oxophilicity, Lewis acidity, and highly reducing nature of U(III) congeners. A new paradigm of such reaction is the addition of different alkynes to \( ^{119}\text{U}^{III}\)(DME) complexes, leading to the immediate formation of vinyl bridged dinuclear complexes of uranium (IV) (cf. below):

Based on those experimental observations, DFT (B3PW91) calculations were conducted, for the prediction of a reasonable reaction pathway. The most thermodynamically favoured and kinetically accessed mechanism consists of two steps: first, oxidation and subsequent formation of the activated dinuclear alkyldiyne complex, followed by cyclization, or C-C coupling, to form the corresponding vinyl bridged dinuclear uranium complex (IV). Alternate pathways, like cyclization of the alkyldiyne in the monomer, were examined as well, in order to conclude which one will be the most favoured one. Moreover, we have investigated a possible C-H activation process, to verify the correctness of our predicted mechanism, which was found to be kinetically less accessible and thermodynamically unfavored than the first one. In sum, our calculations highlight the generality of this particular mechanism and shed light to different ways of extending the applicability of our mechanism to less active olefins.
Multi-colour emission from embedded luminescent nanoparticles in KTiOPO₄ micro-structures for laser phosphor display applications


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In the last few years, a passionate interest has been growing for controlling the electromagnetic radiation by focusing on patterned structures and materials, especially when the dimensions of the structured material match the wavelength for resonant optical processes. However, light distribution control can also be achieved using patterned structures at the micrometer level, an interesting topic that has been minimally explored. A particularly interesting approach has been the control of light distribution spatially and spectrally generated by optically active trivalent lanthanide (Ln³⁺) ions. It has been demonstrated that by embedding Ln³⁺-doped nanoparticles into microstructured materials it might be possible to control the light spatially at the micrometer scale in a wide spectral range [1].

This kind of technology might have interesting implications to reinforce the emerging technology of laser phosphor displays (LPD). Here we present the fabrication of new luminescent composites to be used in this technology that use IR excitation and up-conversion emission mechanisms instead of the UV excitation used in present devices. The luminescent composites are formed by a high laser damage substrate material, KTiOPO₄, whose surface has been structured with one-dimensional (1D) and two-dimensional (2D) ordered arrays of grooves and holes by means of ultrafast laser ablation. Then, these grooves and holes have been filled with luminescent nanoparticles of KYb(WO₄)₂ doped with different lanthanide ions to get red, green, and blue emissions to generate RGB LPD panels.

**Figure 1.** Luminescent intensity map generated by Er:KYb(WO₄)₂ nanoparticles embedded in a 2D array of holes in KTP.

Bis(phosphinimino)methanide borohydride complexes of rare-earth elements as initiators for the ring-opening polymerization of trimethylene carbonate

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Rare earth borohydride complexes are known as efficient initiators for the polymerization of both apolar and polar monomers. Bis(phosphinimino)methanide bisborohydride complexes of lanthanum, yttrium and lutetium, [{CH(PPh2NSiMe3)2}La(BH4)2(THF)] (1) and [{CH(PPh2NSiMe3)2}Ln(BH4)2] (Ln = Y (2), Lu (3)), have been investigated in the ring-opening polymerization (ROP) of trimethylene carbonate (TMC). All three initiators afforded linear poly(trimethylene carbonate)s (PTMCs) in toluene at 23 °C.

Scheme 1  Phosphiniminomethanide rare earth complexes [{CH(PPh2NSiMe3)2}La(BH4)2(THF)] (1) and [{CH(PPh2NSiMe3)2}Y(BH4)2] (2) used in the polymerization of TMC.

Small molecule reduction using uranium(III) and borylation of reduced intermediates

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The chemistry of uranium(III) is dominated by its strongly reducing nature, and much interesting chemistry has been reported based on this.1 Seminal papers have revealed dinitrogen2 and carbon monoxide3 coordination and selective CO coupling at uranium centres.4 We have recently demonstrated previously unsuspected chemistry of uranium tris(aryloxide)s including dinitrogen binding and reduction, as well as reductive coupling of CO to form the ynediolate dianion [OCCO]2-.5 Both uranium tris(aryloxide) and the common uranium(III) starting material [U{N(SiMe3)2}3] also show hydrocarbon activation chemistry and subsequent borylation.6

![Chemical structure diagram]

References
Magnetic properties of a Dysprosium Layered Lanthanide Hydroxide and its intercalation for 2,6-naphtalenedicarboxylate

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Layered materials with composition Ln$_8$(OH)$_{20}$Cl$_4$$\cdot$nH$_2$O (Ln: Eu, Tb, etc.) were originally prepared by Sasaki and coworkers. A host-guest system with pure lanthanide cations in the layer allows us to combine the study of lanthanide chemistry with that of layered and intercalated compounds, providing advances in the field of new organic-inorganic hybrid materials and potentially showing interesting properties derived from multifunctionality. The optical properties of these compounds attracted recently some attention but very little is known about their magnetism.

In this work we report the synthesis and magnetic properties of a dysprosium layered lanthanide hydroxide, Dy$_8$(OH)$_{20}$Cl$_4$$\cdot$6H$_2$O (Dy-LLH), and its intercalation product with the 2,6-naphtalenedicarboxylate organic anion, Dy$_8$(OH)$_{20}$(C$_{12}$H$_6$O$_4$)$_2$$\cdot$4.5H$_2$O (Dy-LLH-26-NDC), after direct anion-exchange (Fig. 1).

Figure 1. Schematic representation of the interlayer arrangement of the 26-NDC anion between the Dy-LLH layers.

These compounds present a paramagnetic behavior due to Dy ions in layers. AC magnetic susceptibility measurements at low temperatures for both compounds revealed a significant degree of magnetic relaxation in the absence of external field (Fig.2). For Dy-LLH, an energy barrier of 28.5 K was obtained and the onset of tunneling regime is visible below 4 K, providing clear evidence of behavior as a two-dimensional magnet.

Figure 2. Temperature dependence of both components (real $\chi'$ and imaginary $\chi''$) of the AC susceptibility for the Dy-LLH compound.

Diamine bis-phenolates as supporting ligands in organoactinide (IV) chemistry

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We are interested in the preparation of non-cyclopentadienyl organoactinide complexes as a result of their largely unexploited potential in both traditional organometallic catalysis and in the development of novel reactivities. Diamine bis(phenolate) ligands, in particular the dianionic tetradentate salan-type chelates, are versatile ligands and have proved to be adequate for the stabilization of early transition metal alkyl complexes, used as precatalysts in homogeneous polymerization processes.[1,2]

These ancillary ligands have never been explored with respect to thorium (IV) and uranium (IV) centers up to now. We will present our recent results showing that the [salan-tBu2]2− ligand is adequate for the synthesis of mono-ligand complexes of general formula [AnIV{salan-tBu2}X2L] (An = Th, U; X = Cl, I; L = dme, 2,2′-bipyridine).

These complexes were prepared by reacting ThCl4(DME)2 or UX4(L)n (L = Et2O, PhCN) with the respective potassium salt in the presence of a bidentate co-ligand. Reacting AnX4 with K2[salan-tBu2] in 1:2 molar ratio led to the formation of the bis-substituted compounds [An{salan-tBu2}2] (An = Th, U). Moreover, we will show that these complexes provide useful starting materials for the synthesis of new alkyl complexes of actinides. Salt metathesis reactions of the bis(halide) actinide complexes with LiCH2SiMe3 led to the formation of the bis(alkyl) complexes (ex: Figure 1), which are the first actinide (IV) alkyl complexes anchored on a diamine bis(phenolate) ligand. The complexes were characterized by NMR techniques, ESI/QITMS and by X-ray diffraction analysis.


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Towards Hydrocarbon Activation by Rare-Earth Metal N-heterocyclic Carbene Complexes

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A select group of organometallic rare-earth complexes are known to activate small molecules such as methane.\textsuperscript{1} However, as these rare-earth complexes are redox inactive, further chemistry is limited. In recent years our group has synthesised bidentate, saturated N-heterocyclic carbene (NHC) ligands bearing anionic alkoxide tethers. These allow the hemilabile carbene donors to be retained in the coordination sphere of the electropositive metal.\textsuperscript{2} We have demonstrated that in organo rare-earth complexes this hemilabile NHC can act as a reactive donor ligand and allow these redox inactive metals to partake in further chemistry.\textsuperscript{3}

Scheme (1): Formation of C-Si bonds from the addition of halosilanes to rare-earth carbene complexes

Two functional groups can be delivered simultaneously to an organometallic rare-earth complex via the addition of an E-X (E = SiR\textsubscript{3}, PR\textsubscript{2}, SnR\textsubscript{3}, X = halide) across the metal-carbene bond to form a zwitterionic imidazolinium metal complex with E adding to the carbene and X to the metal. Upon warming to room temperature functionalised hydrocarbyl compounds (ER) are spontaneously eliminated from the complex reforming the metal-carbene bonds.\textsuperscript{4}

We will present the synthesis and reactivity of a number of rare-earth aryloxide and other alkyl complexes in order to expand the scope of this addition-elimination chemistry.

Increasing solar energy conversion by Eu$^{3+}$ and Bi$^{3+}$ co-doped La$_2$O$_3$ nanocrystals as a down-shifting material

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For the past few decades, solar energy converters based on silicon have become dominant in solar cell technology. However, the high production cost and sophisticated fabrication process have propelled researchers to look for environmentally-friendly, cost-effective and simpler fabrication processes based on polymeric materials. From another side, polymer-based solar cells suffer from the bandgap absorption of these materials, typically below 2eV which limits their efficiency. In order to enlarge the absorption range of polymer-based solar cells and enhance their efficiency, new materials, especially with nanosizes and absorbing in complementary regions of the electromagnetic spectrum and emitting in the absorption range of semiconducting polymers, are being investigated at present.

We propose to use 5 mol% Eu$^{3+}$ and 1mol% of Bi$^{3+}$ co-doped La$_2$O$_3$ nanoparticles (Eu$^{3+}$:Bi$^{3+}$:La$_2$O$_3$) as a down-shifting (DS) material to enhance the efficiency of the bulk heterojunction solar cells. The motivation for using materials containing rare-earths as DS material is that this family of elements show luminescent properties over a wide range of wavelengths, extending from the near-infrared, through the visible and the ultraviolet (UV). Thus, these materials can absorb in the regions of the electromagnetic spectrum in which polymeric solar cells cannot absorb, such as UV, and convert them in emissions in the visible that can be easily absorbed by the polymers.

![Figure 1a) TEM image of the Eu$^{3+}$:Bi$^{3+}$:La$_2$O$_3$ nanoparticles and b) their spectroscopic properties.](image-url)
The design of multinuclear molecular actinide complexes is of high current interest because of their efficiency to provide practical models to understand the uranium mobility in the environment and to investigate the magnetic interaction and the electronic structure of actinide materials. Accordingly we have become interested in studying the chemistry of pentavalent actinyl (AnO$_2$$^+$) compounds. A key property of an actinyl(V) moiety is its ability to bind to another actinyl moiety through the axial oxygen (commonly known as cation-cation interaction, CCI). While the study of actinides like Np and Pu is limited by their high radioactivity, UO$_2$$^+$ provides an easy-handling isostructural model to these compounds. The synthesis of stable pentavalent uranyl complexes presenting CCI’s provides a route to the self assembly of multinuclear uranium complexes trough the mutual coordination of the UO$_2$$^+$ groups, and allows a better targeting for the synthesis of their neptunyl and plutonyl analogues. We have thus recently shown that a suitable choice of ligand and conditions can lead to the isolation of multinuclear complexes of pentavalent uranyl with different nuclearities$^{1-5}$. On the other hand, the recent isolation of an analogous neptunyl(V) starting material$^{6}$ provides a convenient way for the access to new multinuclear neptunyl assemblies. The structure and properties of these polymetallic assemblies of uranyl(V) and neptunyl(V) will be presented.

Lanthanide based complexes are very interesting compounds due to their original optical and magnetic behavior. If the transitions corresponding to these properties are entirely attributed to the cationic metal, the choice of the ligand and of the chemical environment is crucial. Indeed, depending on the denticity of the ligand for example, lanthanide complexes can be used in applications such as imaging\textsuperscript{1} or diagnosis. Meanwhile, concerning their luminescence properties, the use of a photosensitizing agent is strictly required, in order to realize an indirect excitation.

We were interested in the development of new ligands displaying various spectral properties, by the association of a central pyridine to different aromatic rings, providing several highly conjugated fragments able to sensitize efficiently lanthanide ions such as Europium and Terbium.

In addition, due to the oxophilicity of those trivalent ions, phosphonated moieties were covalently attached to the organic chromophores, and the following acyclic nonadentate ligands were synthesized:

For each of them, the organic synthesis and the very interesting photophysical properties of Eu and Tb complexes will be presented.

A Chiral Probe for Alpha-1-Acid Glycoprotein Based on Europium Luminescence

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The serum protein $\alpha$-1-acid glycoprotein ($\alpha_1$-AGP) is an important acute phase protein whose concentration rises by up to 400% as a result of inflammation in several disease states. It binds strongly to a variety of non-polar and basic drugs (e.g. chlorpromazine, methadone, Glivac, warfarin), regulating their pharmacokinetics. As part of a study aimed at developing chiral luminescent probes we have identified a dynamically racemic europium(III) complex as a probe for this protein, suitable for use in human serum. Binding of $\alpha_1$-AGP is characterised by a major variation in the spectral form of Eu emission ($\phi_{em} = 18\%$), consistent with a change in the Eu coordination environment. Complexation is also signalled by strong induced circular dichroism into the ligand chromophore and intense circularly polarised luminescence from the metal centre ($g_{em} = 0.4$). Affinity constants have been measured for six of the most abundant serum proteins, with $\alpha_1$-AGP binding most strongly by over an order of magnitude ($K_d = 1.5 \mu$M). Each protein-bound complex gave characteristic Eu emission and CPL profiles allowing identification of the main protein-bound species in mixtures. Using emission spectral changes and ratiometric methods, it has been possible to calibrate the intensity ratio change to report the elevation of $\alpha_1$-AGP levels in human serum directly.

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Aryl-phosphonate lanthanide complexes as multimodal imaging probes

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Lanthanide complexes have great potential to be utilised as contrast agents in a variety of different imaging modalities. Depending on the characteristics of the incorporated ion such complexes could find application in optical or magnetic resonance imaging. To fully exploit their unique optical and magnetic properties ligand systems should be designed with structural features that mutually accommodate the imaging requirements of these ions, where the application of a cocktail of different complexes of the same ligand system could provide multiple signals to be detected simultaneously.

Recently, we synthesized and investigated a series of aryl-phosphonate appended macrocyclic complexes, which display high relaxivities (Gd$^{3+}$ complexes) and long lived sensitized emissions with high quantum yields (Tb$^{3+}$ complexes). The strong MR signal was retained at high field strengths, in model extracellular medium and in cellulo. Phantom MR measurements for the latter revealed a reduction in apparent relaxivity for three of the complexes coinciding with a reduction in extracellular volume. Following incubation and washing, an enhancement in the contrast was observed for one system, indicating the system was interacting or internalising.

To improve the imaging capabilities of these systems, we incorporated a fluorinated group on the aryl moiety to provide an additional signal to be detected through $^1$H and $^{19}$F MRI. By incorporating different lanthanide ions (Eu$^{3+}$, Gd$^{3+}$, Tb$^{3+}$ and Yb$^{3+}$), we could observe strong luminescence and multifrequency MR signals.

Hyperfine constants DFT calculations for MRI

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Magnetic resonance imaging \cite{1}, used particularly for cerebral tumors diagnostic, is a non-invasive technique with a sub-millimeter spatial resolution. This high accuracy is due to the use of contrast agents, which are mostly gadolinium complexes.

The efficiency of contrast agents is based on the optimisation of the NMR relaxation time of water protons surrounding these molecules. The calculation of the longitudinal relaxation time $T_1$ with an \textit{ab initio} method would be the ultimate goal of any theoretical study. This relaxation process is induced by the time fluctuations of hyperfine interactions between the electronic spin located on the gadolinium ion and the nuclear spin of the water protons \cite{2}, and it is therefore crucial to compute them with a good accuracy.

This task becomes quite difficult because of the presence of unpaired $4f$ electrons and of relativistic effects. Moreover, the level of calculation and the environment (i.e., solvation) do play a significant role. Different tests have therefore been performed to determine the best approach in terms of accuracy and computation time. Afterwards, hyperfine tensors have been calculated along a Car-Parrinello trajectory\cite{3}\cite{4}\cite{5}. Preliminary results have reveal that the hydrogen-bonds network around the coordinated water molecule also influence the hyperfine interactions tensors.

Interaction of Cm(III) and Eu(III) with a water-soluble BTP-type ligand

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Separation of long-lived radionuclides from spent nuclear fuel, with subsequent conversion into shorter lived or stable nuclides by fast neutron induced fission reaction, is a promising concept to reduce the long term radiotoxicity of high level nuclear waste\textsuperscript{1}. This concept is designated as partitioning and transmutation strategy.

The most critical part is the Selective Actinide Extraction step (SANEX), where the trivalent minor actinides Americium and Curium have to be separated from the chemically very similar fission lanthanides. An efficient separation process requires highly effective extracting agents. Soft heterocyclic N-donor ligands such as functionalized bis(1,2,4-triazin-3-yl) pyridines are among the most promising candidates for selective extraction of trivalent actinides from nitric acid solutions\textsuperscript{2}. Hydrophilic aq-BTP, a further development of the common hydrophobic BTP ligands, is used as aqueous complexing agent for the selective back extraction of actinides from organic phases loaded with trivalent actinides and lanthanides\textsuperscript{3}.

In order to get a better insight on a molecular level, complex formation is followed by time-resolved laser fluorescence spectroscopy (TRLFS). TRLFS is a very sensitive speciation method that allows in-situ speciation of actinides/lanthanides in the submicromolar concentration range\textsuperscript{4}. Cm(III) and Eu(III) as representatives for the trivalent actinides/lanthanides exhibit excellent spectroscopic properties and can therefore be used as a luminescence probe to study the coordination chemistry of aq-BTP.

Under the presence of increasing amounts of aq-BTP the three M(III) complex species $[\text{M(aq-BTP)}_n]$ (M=Cm(III)/Eu(III); $n = 1,2,3$) were identified and spectroscopically characterised. Peak deconvolution was used to determine the species concentrations and stability constants, required for future process development, were derived. Furthermore, strong energy transfer processes between the aq-BTP ligand and the metal cations, resulting in exceptionally high fluorescence intensity factors were observed. Complexation studies at different temperature gave information on the entropy and enthalpy of complex formation.

References:

Temperature Dependent Photoluminescence of Triply Doped (Ho,Tm,Yb):KLu(WO$_4$)$_2$ single crystal

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There has been extensive interest in the study of lanthanide doped materials for use as temperature sensors. In these materials many pairs of energy levels with small energy separations and thermally coupled are known that can be used for this purpose. Optical temperature sensors can reduce the dependence of measurement condition and improve the sensitivity by measuring the fluorescence originated from f → f transitions in lanthanide ions.

Up to now, only Er$^{3+}$ doped and Er$^{3+}$-Yb$^{3+}$ codoped materials have been used with this purpose monitoring green upconversion emission through the $^2H_{11/2}$ and $^4S_{3/2}$ energy states that are thermally coupled. Here, we extend this methodology to other ions that can be sensitized by Yb$^{3+}$, that absorbs in the IR and transfers effectively its energy to Er$^{3+}$, Tm$^{3+}$ and/or Ho$^{3+}$ to generate visible emissions by upconversion processes.

We studied the temperature dependent luminescence in (1% Ho, 0.5% Tm, 1% Yb):KLu(WO$_4$)$_2$ monoclinic crystal with emissions in the blue, green and red of the electromagnetic spectrum [1]. KLu(WO$_4$)$_2$ is a well know host material for lanthanide ions belonging to the family of monoclinic double tungstates, that are characterized by presenting high absorption and emission cross sections for these active ions in this matrix. Spectra were recorded in the temperature range 295 K – 673 K. It was found that the intensities of all the bands decrease with increasing temperature (Fig.1). We observed a dual behavior of this material at low and high temperatures, as well as two thermally coupled energy levels belonging to two different lanthanide ions.

![Figure 1: Emission spectra of (1% Ho, 0.5% Tm, 1% Yb):KLu(WO$_4$)$_2$ single crystal in range of temperatures from 295 to 573 K.](image)

The 1.9 μm laser emission corresponding to $^{3}F_4 \rightarrow ^{3}H_6$ transition of Thulium (Tm$^{3+}$), is very interesting for applications in medicine and atmospheric sensing mainly because the high absorption of water in tissues and CO$_2$ and water in the atmosphere. A wide variety of hosts have been served for Tm as active ion, among them are the garnets (YAG, YALO), vanadates (YVO, GdVO and LuVO), fluorides (YLF, LuLiF, GdLiF) sesquioxides (LuO, ScO) and monoclinic double tungstates (KYW, KLuW, KGdW) to name a few. High powers and high efficiencies have been achieved using these hosts in diode-pumped (DP) configuration and continuous-wave (CW) regime.

Tm-doped monoclinic double tungstates (with general formula $KRE(WO_4)_2$), offer great advantages such as: high absorption and emission cross-sections, the possibility of high doping levels without significative fluorescence quenching and long upper level lifetimes, interesting for pulsed regimes. Among tungstates, the potassium lutetium double tungstate (KLuW) shows the highest output power (max. 4 W in CW) and highest efficiency (69% with respect to the absorbed power) in DP configuration [1].

Passive Q-switching (PQS) techniques offer low-cost and compactness of the laser system to generate pulses of the order of nanoseconds durations. The PQS relies on the use of an intracavity saturable absorber (SA) which must have high absorption at the laser emission and low upper lifetime compared to the upper laser lifetime of Tm. Few works have been addressed in this line, for instance in Tm:YAG [2] and Tm:KYW [3] using Cr$^{2+}$:ZnS and Cr$^{2+}$:ZnS crystals, PbS quantum dots, and InGaAs/GaAs semiconductor based SAs.

Concerning the isostructural KYW, an average output power of 116 mW at a repetition rate of 20 kHz resulting in a single pulse energy of 6.7 μJ and pulse duration of 63 ns have been achieved in the codoped Tm,Yb:KYW using Cr$^{2+}$:ZnS as SA. More recently, PQS of Tm:KYW has been achieved also using PbS-doped glass as SA [4]. In this set-up, up to 44 μJ of single pulse energy was produced at a repetition rate of 2.5 kHz but for the pulse duration only an upper detection limit of 60 ns was given.

In this work, we substantially improved the results of PQS regime in Tm:KLuW laser at 1920 nm, achieving a maximum average output power of 390 mW at a repetition rate of 2.7 kHz resulting in 145 μJ pulse energy with pulse durations around 30 ns resulting in peak powers as high as 6 kW, using Cr:ZnS poly-crystalline samples as SA,s.

A macrocycle-appended naphthalimide derivative and its Eu(III) complex show triple luminescence from isolated naphthalimide units (blue), aggregated naphthalimide excimers (green), and Eu centres (red) with the balance being sensitive to the degree of aggregation, allowing white light emission to be obtained from a single molecule.¹

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UPCONVERTING LANTHANIDE DOPED ALKALINE EARTH FLUORIDE NANOPARTICLES

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Fluoride based materials doped with lanthanide ions are interesting hosts for efficient luminescence, also because they can be prepared in colloidal forms, thus opening the doors to their use in important technological applications, especially in biomedical diagnostics [1]. Lanthanide doped CaF₂ nanoparticles (NPs) very recently have raised attention, due to their strong upconversion (anti-Stokes) emission [2-4].

A facile hydrothermal one-step procedure was used to prepare citrate capped MF₂ (M=Ca, Sr) NPs codoped with Tm³⁺/Yb³⁺ ions. These NPs are easily dispersible in saline solution, while maintaining the upconversion properties.

The structural and morphological properties of the lanthanide doped NPs were investigated by X-Ray diffraction and electron microscopy. The obtained nanocrystalline materials (see Figure 1) are single phase and can be easily dispersed in physiological solution. The colloidal solutions show strong upconversion emission upon laser excitation at 980 nm in the ²F₅/₂ level of Yb³⁺ (see Figure 2).

![Fig. 1. TEM image of SrF₂ nanoparticles](image)

![Fig. 2. Upconversion spectra and pictures of colloidal dispersions of Tm³⁺, Yb³⁺ codoped CaF₂ and SrF₂ nanoparticles (λ_exc=980 nm).](image)

Luminescent lanthanide containing compounds find niche applications as fluorescent labels in biological imaging and dopants for fiber amplifiers, lasers and optoelectronic devices. The longevity and internal quantum efficiencies of the excited states can be optimised by the employment of multidentate chelating ligands that satisfy the coordination preference of a given ion and/or by perfluorination of the ligands to exclude inner sphere solvent molecules and limit detrimental vibrational quenching mechanisms.\textsuperscript{1} Here, we describe our efforts towards the development of a family of fully perfluorinated visible and near IR emitting lanthanide complexes that exhibit particularly long luminescent lifetimes in solution.\textsuperscript{1} The potential applications of these complexes will also be explored.

Local structure of Lanthanide’s doped Tetravalent Nano-oxides

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This presentation includes our recent results on the lanthanide’s doped tetravalent nano-oxides, namely CeO2, ZrO2 and CeO2-ZrO2. These materials attract tremendous attention as advanced ceramics, catalysts, sensors and luminescent materials. Such applications rely on their unique, but very poorly understood, structures and physical properties. The broad aim of our research is to identify, describe and provide novel insights on the structure-luminescence relationships occurring in these oxides. The approach used in investigation is based on the unitary investigation of their luminescence and structural properties.

Our work is based on the application of complimentary techniques and methods such as high resolution transmission and scanning electron microscopies, in-situ RAMAN and X-ray diffraction, X-ray photoelectron spectroscopy and luminescence spectroscopy. At the heart of the investigation are the temporarily and spectrally resolved luminescence studies. In this talk, we present some of our recent results which make use of europium as luminescence probe with an emphasis on the dopant distribution and surface properties, order and disorder effects and nanoscale inhomogeneities in CeO2-, ZrO2 and CeO2-ZrO2.

References
The development of novel, structurally defined supramolecular self-assemblies and functional nanomaterials is of great current interest. Besides being an important component of microelectronic, magnetic and optical devices, such nanostructures can be successfully used in bio-related applications. Owing to their biocompatibility, unique size- and shape-dependence and moreover their relatively simple, but successful functionalisation with different organic molecules, gold nanoparticles (Au NPs) are particularly well-suited for this purpose.

The objective of the work presented in this poster consists in the design and synthesis of Au NPs functionalised with lanthanide (Ln) cyclen complexes for the development of new targeting probes acting as luminescent tags for sensing or imaging. The combination of the unique spectroscopic properties of the Ln’s (long-lived excited states, large stoke’s shift, line-like emission) and the use of Au NPs for luminescent sensing and cellular imaging, to the best of our knowledge, has not been much explored to date.[1]

We thank IRCSET and SFI for funding.

The recently introduced superbulky cyclopentadienyl ligand CpBIG exhibits unique properties.\[1\] Attempted synthesis of half-sandwich Sm\textsuperscript{III} and Yb\textsuperscript{III} complexes (CpBIG)\textsubscript{2}SmR\textsubscript{2} and (CpBIG)\textsubscript{2}YbR\textsubscript{2} (R = 2-dimethylamino-benzyl) resulted in spontaneous reduction to the Ln\textsuperscript{II} full-sandwich complexes (CpBIG)\textsubscript{2}Sm and (CpBIG)\textsubscript{2}Yb.\[1\] Half-sandwich complexes of Y, Dy, Nd and Tm could be obtained and were crystallographically characterized.

However, the high solubility of these complexes renders crystallization difficult and results in diminished product yields. For this reason we introduced a "castrated" version of the original CpBIG ligand, abbreviated CpBIGc. In contrast to CpBIGH the CpBIGcH ligand can be obtained by a simple synthetic procedure which can be easily scaled up to 100 g quantities.\[2\] The significantly reduced solubility of CpBIGc complexes compared to CpBIG complexes greatly simplifies crystallizations. Herein we describe the synthesis of CpBIGc lanthanide complexes and preliminary results in reactivity studies and catalytic applications.

\[2\] B. Martin-Matute, M. Edin, K. Bogár, F. Betül Kaynak, JACS 2005, 127, 8817
Self-assembled heteropolymetallic complexes as potential agents for bimodal imaging

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Multimodal imaging agents are gaining nowadays great attention in the field of clinical and preclinical imaging applications. Whereas MRI is ideal for whole body images due to its good spatial resolution, its sensitivity is rather low so that millimolar concentrations of Gd(III)-based contrast agents are required. Luminescence-based imaging, on the other hand, can provide high-resolution images but this technique is only suitable for thin tissue samples because of the low optical transparency of biological tissue. Because biological samples strongly absorb at UV and visible wavelengths, suitable metal complexes for luminescence-based imaging are restricted to those showing emission in the red end of the visible spectrum and in the near-infrared (NIR) because radiation of these wavelengths can more easily and effectively penetrate tissues. Although multimodal imaging agents are developing at a growing pace, reports dealing with the design of f-d heterometallic systems for this purpose remain quite scarce.

Our approach in achieving such goal is reflected in the design of novel ditopic ligands capable of coordinating both f and d metals. These ligands contain a DTPA-derivative as a binding unit for the lanthanide(III) ion on one hand and a catechol, a 8-hydroxyquinoline or a 1,10-phenanthroline derivative as a binding unit for d- or p-metal ions. Binding of those metals such as Ru^{2+}, Ti^{4+}, Al^{3+}, Ga^{3+} results in formation of a heteroplymetallic complex with improved relaxivities and optical properties. Relaxometric and luminescent properties of Gd^{3+} complexes have been studied in detail, as well as their ability to bind to Human Serum Albumin (HSA). In addition, the Eu(III) analogous have been prepared and investigated in order to gain information about the coordination environment and solvation numbers of the lanthanide(III) ions.

Towards the functionalisation of coupled carbon monoxide by uranium(III) complexes

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The $\text{C}=\text{O}$ bond is the strongest diatomic known, yet it is a major industrial feedstock for the formation of many bulk and fine chemicals through the formation of C-C bonds. This requires a significant energetic contribution and the use of catalysts. We have recently shown that it is possible to reductively couple carbon monoxide with a common uranium tris(amide) coordination complex, to yield the linear ynediolate dianion $[\text{OCCO}]^{2-}$ under ambient conditions. This has been achieved nearly 200 years ago in the form of explosive potassium salts and also very recently by another organometallic uranium(III) compound under carefully controlled conditions.

The first example of further reactivity of the ynediolate core is demonstrated when $\text{N”}_3\text{UCCOUN”}_3$ is heated to 80 °C forming a seven-membered metallacyclic ring containing an alkene bond from the formal addition of a silyl methyl C-H across the alkyne. (Scheme 1)

![Scheme 1](image)

Scheme 1: Coupling of CO by $\text{UL}_3$ and subsequent formation of a metallacycle when $L = \text{N”}$

$\text{U(OAr)}_3$ ($\text{OAr} = 2,6$-di-tert-butylphenoxide or $2,4,6$-tri-tert-butylphenoxide) exhibits similar reactivity to the tris(amide) but has a number of advantages over the amide system.

We will show our progress in the search to find a reagent which can remove the coupled diolate core from these complexes to produce functionalised small $\text{C}_2$ molecules and allow the development of the first catalytic cycle for coupling CO.
Separation of actinides and lanthanides by zirconium phosphate ion exchangers

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Partitioning and transmutation (P&T) of long-lived nuclides is a part of the research on nuclear fuel waste treatment. Inorganic ion exchangers with high radiation resilience offer an alternative or is complementary to solvent based extraction methods in actinide and lanthanide radiochemical separation. The aim of this study is creating such exchangers for to be used for nuclide separation either directly in nitric acid dissolved fuel or in the secondary wastes created by currently used hydrometallurgic processes such as PUREX or its derivatives. α-Zirconium phosphate and γ-zirconium phosphate has been synthesized. Distribution coefficients (K_D) for the model elements used, europium-152 and americium-241, have been determined in nitric acid solutions of different molarities by batch experiments. Pure zirconium phosphates have been characterized by powder x-ray diffraction (PXRD) and further characterization will be conducted for Am- or Eu-loaded exchanger to possibly have an understanding about the exchange sites and their selectivity towards these nuclides. Ion exchange chromatographic experiments have been started with the aim to separate our model elements from each other by optimizing elution conditions. Unoptimized, preliminary tests show promise for the separation. γ-Zirconium phosphate, which offered best separation according to the determined K_D-values, is powder-like on its own and have been bound to silica in order to increase crystallinity and grain size for it to be suitable for column separation. Fig 1 shows the determined K_D-values for α-zirconium phosphate (ZrP-1), γ-Zirconium phosphate (ZrP-2) and high purity α-zirconium phosphate (ZrP-3). The difference between ZrP-1 and ZrP-3 is that ZrP-1, according to [1], contains 15-20 % of solid phosphoric acid.

1. C. Trobajo, Chem. Mater. 2000, 12(6), 1787
The early actinides are known to exist as linear dioxo, or ‘yl’, species in high oxidation states. For uranium, the most prevalent species is uranyl(VI) (\{UO_2\}^{2+}) which is the more stable and therefore the most well understood oxidation state. However, uranyl(V) has also been shown to play an important role in the bioremediation of uranium in the environment, but is generally unstable with respect to disproportionation. In solution, it readily forms U(IV) and UO_2(VI), thought to proceed by inner sphere electron transfer mediated by uranium–oxo-uranium interactions.

The aim of this project is to develop further understanding of the uranyl(V) unit and to utilise time resolved luminescence spectroscopy to follow disproportionation events in solution. The synthesis of a family of neutral polypyridyl ligands bearing bulky silyl groups will be described and their coordination chemistry with uranium discussed.\(^1\) We will also describe the synthesis and photophysical properties of uranyl(VI) oligomers assembled by uranyl-oxo-uranium electrostatic interactions with anionic O donor ligands and investigate routes to their uranyl(V) analogues.

Phosphorus-Stabilised Rare Earth Carbenes

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Previously we have reported the synthesis of rare earth tribenzyls \([\text{Ln}(\text{Bn})_3(\text{THF})_3]\) (\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Dy}, \text{Er}, \text{Y}; \text{Bn} = \text{CH}_2\text{Ph}) and have utilised these complexes in the synthesis of lanthanide carbone complexes, \([\text{Ln}(\text{BIPM}^{\text{TMS}})(\text{Bn})(\text{THF})]\) \([\text{BIPM} = \{\text{C}(\text{PPh}_2\text{NSiMe}_3)_2\}_2\}^2\] and \([\text{Ln}(\text{BIPM}^{\text{TMS}})(\text{BIPM}^{\text{TMS}}\text{H})]\). [1] We have targeted analogues of these complexes with iodide in place of alkyl groups due to their greater synthetic utility. Complexes 1a-b were synthesised by reaction of \([\text{Ln}(\text{I})_3(\text{THF})_{3.5}]\) with two equivalents of \([\text{K}(\text{Bn})]\) and subsequent reaction with \text{BIPM}^{\text{TMS}}\text{H}_2\) yielded \([\text{Ln}(\text{BIPM}^{\text{TMS}})(\text{I})(\text{THF})_2]\), 2a-b (\text{Ln} = \text{Y}, \text{Er}). [2] Reaction between 2b and \([\text{Ga}(\text{NArCH})_2][\text{K}(\text{tmeda})]\) (\text{Ar} = 2,6-diisopropylphenyl) yielded 3, a heterobimetallic complex containing an unsupported Er-Ga bond. The synthesis of a dysprosium analogue of 1a-b proved unsuccessful due to ligand scrambling in Schlenk-type equilibria, while attempts to prepare analogues of 2a-b for larger lanthanides via salt elimination have proven problematic, but are a future synthetic target. [3]

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